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A TEXTBOOK OF PHYSICS

BY

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VOL. II

HEAT AND SOUND

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FROM THE PREFACE TO THE SEVENTH GERMAN EDITION

The success of this textbook has been due primarily to Grimsehl's remarkable gifts as a teacher. Amplified after his death in the spirit of the original, the work has obtained widespread recognition and is in extensive use both as a reference book for teachers and also as a textbook for students at universities and technical colleges.

While preserving the original character of the book, it has been possible to take account of the new advances as well as of the changes in treatment and arrangement of the subject-matter which these advances necessitate. Care has been taken not to exceed the previous scope of the book. Certain parts of major importance, notably in the section upon electricity, have had to be completely rewritten.

My thanks are due to Dr. Stehberger and also to Dr. Schauff (who was chiefly concerned with the editing of the school edition of Grimsehl's work) for their kind assistance in reading the proofs. I should also like to thank all those who have helped by letting me have diagrams and original photographs.

I wish to express my gratitude to the publishers for their sympathetic co-operation with regard to the new illustrations.

R. TOMASCHEK.

MARBURG ON THE LAHN,

August, 1929.

PREFACE TO THE ENGLISH EDITION

I have taken the opportunity of the publication of this edition to make a few corrections and improvements. With a view to meeting the needs of English readers, some new matter has been added. I wish to thank the translator for the adequate manner in which he has carried out his task, and hope that in its new dress the work will greatly extend the circle of its friends.

R. TOMASCHEK.

MARBURG,
7th Feb., 1933.

The English publishers wish to express their thanks to the authorities of the Royal Society and to Dr. J. K. Roberts for permission to use diagrams which have appeared in the Philosophical Transactions and in the textbook Heat and Thermodynamics by Dr. Roberts.

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HEAT

CHAPTER I

Thermometry. Specific Heat. Heat and Work

1. Thermometers

1. **Temperature. Thermometers.**—Most bodies expand when heat is added to them and contract again when heat is removed from them. If the amount of heat taken away is equal to that previously added, a body will return once more to its original volume. The volume of a solid body or a given amount of liquid is constant so long as its **thermal condition** (temperature*) remains unchanged. Hence this volume can be used as an indicator for the corresponding thermal state. The volume of a given mass of gas is also suitable for this purpose provided that the pressure is constant.

A device in which the change of volume of a body is used to indicate changes of temperature is called a **thermoscope**.† When the change of volume is used as a *measure* of the thermal state, the instrument is called a **thermometer**.‡

If a glass vessel fitted with a narrow exit tube at the top be filled up to this tube with a liquid, the free surface will rise visibly in the tube when the vessel and its contents are warmed slowly. From this it follows that the volume increase (cubical expansion) of the liquid is greater than that of the vessel. At each temperature the liquid stands at a quite definite level in the tube. Hence *this level can be used as an indicator* for the corresponding temperature. Of all liquids *mercury* has proved to be the most suitable for the measurement of temperature.

2. **Mercury Thermometers. Fixed Points.**—The **mercury thermometer** (fig. 1) consists of a narrow closed glass tube of uniform bore (the stem) with a bulb blown at one end. The bulb and a part of the stem are filled with mercury, the remainder of the closed tube being usually air-free.

* Lat., *temperare*, to temper. † Gr., *thermós*, hot; *skopein*, to see.

‡ Gr., *metrón*, measure. The name thermometer can be traced back as far as 1628.

When the instrument is placed in melting ice the mercury level takes up a certain position. This is always the same however often the experiment be repeated (but see p. 4). In the same way the mercury is at another definite level when the thermometer is held

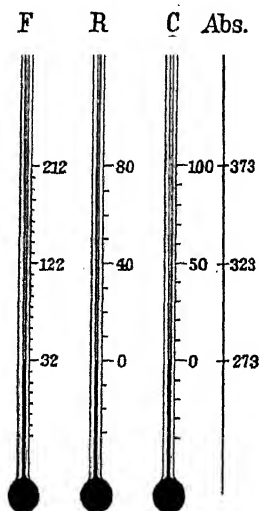


Fig. 1.—Fahrenheit, Réaumur and Centigrade Mercury Thermometers with their Fixed Points.

in the vapour of water boiling at 760 mm. pressure. Thus at normal atmospheric pressure the temperatures of melting ice and boiling water are constant. The two corresponding points on the mercury thermometer scale are called the **fixed points** (the melting-point of ice and the boiling-point of water*). The interval between them may be called the **fundamental interval**. Assuming that the bore of the thermometer stem is uniform, the fundamental interval (and hence also the volume of the stem between the fixed points) is divided into 100 equal parts. Each of these is called a degree.† The lower fixed point is marked 0° C. and the upper one 100° C. (Thus ice melts at 0° C. and water boils at 100° C. under 760 mm. pressure.) The scale divisions are extrapolated at equal distances above and below the fundamental interval and numbered accordingly. Under 0° C. the degree markings are *negative*.

3. Historical.—Thermometers were discovered shortly after 1600 by GALILEO and also independently by the Dutchman DREBBEL. The scale divisions were at first arbitrary. About 1660 the Florentine *Accademia del Cimento* used alcohol thermometers whose scale registered 11° to 12° in the most severe cold of the Tuscan winter, $13\frac{1}{2}^{\circ}$ in melting ice, and 40° in the hottest summer sunshine. These Florentine thermometers were widely distributed at that time. Many suggestions for improvement and comparable production have subsequently been made.

FAHRENHEIT‡ was the first to use mercury as thermometric substance. He chose it after many thorough experiments because only with this substance did he find it possible to make different thermometers giving *results in agreement with one another*. The alcohol thermometers then in use were very inaccurate and insensitive. FAHRENHEIT originally chose the temperature of a freezing mixture of snow and ammonium chloride as the zero of his scale; this was equal to the lowest temperature at Danzig in the winter of 1709. He set blood heat equal to $8 \cdot 12 = 96^{\circ}$. Thus the freezing-point of water lay at about 32° on his scale. He later put this exactly equal to 32° and used it as a fixed point along with the boiling-point of water, which he took as 212° .

* The former was introduced as a fixed point by HOOKE in 1664, and the latter by HUYGENS in 1665.

† Lat., *gradus*, step.

‡ FAHRENHEIT, born 1686, died 1736 at Danzig.

RÉAUMUR * used dilute alcohol as thermometric substance. He originally put the melting-point of ice as 1000° and the boiling-point of water as 1080° , but later set them equal to 0° and 80° respectively. He claimed to have found a special method of making comparable thermometers and discarded mercury as thermometric substance. His work nullified the advances which FAHRENHEIT had made in the measurement of temperature, and the uncertainty in the production of the necessary instruments became greater than ever. Eventually in 1772 DELUC † restored the mercury thermometer to its place of favour. He kept to the Réaumur scale but replaced alcohol by mercury. Thus the Réaumur thermometer ought strictly to be called the Deluc thermometer. It is still used to some extent on the Continent.

After 1740 CELSIUS ‡ took the melting-point of ice as 100° and the boiling-point of water (at 760 mm. pressure) as 0° . He thus introduced the **centigrade scale** into general use, but with the opposite direction from that employed nowadays. The present centigrade scale (i.e. melting-point of ice = 0° and the boiling-point of water = 100°) has been shown to have been first used by LINNÉ || (commonly called *Linnaeus*) in 1740. It is used by all nations. §

4. **Rules for Transformation from one Temperature Scale to Another.**—In the case of Fahrenheit thermometers the melting-point of ice is $+32^{\circ}$ and the boiling-point of water $+212^{\circ}$. The interval between the fixed points is thus divided into 180 degrees. The formulæ for transforming from one scale to another (C. = centigrade, R. = RÉAUMUR, F. = FAHRENHEIT) are:

$$t^{\circ} \text{ C.} = \frac{5}{9} t^{\circ} \text{ R.} = \left(\frac{9}{5} t + 32 \right)^{\circ} \text{ F.},$$

$$t^{\circ} \text{ R.} = \frac{5}{9} t^{\circ} \text{ C.} = \left(\frac{5}{9} t + 32 \right)^{\circ} \text{ F.},$$

$$t^{\circ} \text{ F.} = \frac{5}{9} (t - 32)^{\circ} \text{ C.} = \frac{5}{9} (t - 32)^{\circ} \text{ R.}$$

More succinctly, if C, R, F are the numbers representing a given temperature on the three scales, then

$$\frac{C}{5} = \frac{R}{4} = \frac{F - 32}{9}.$$

It has been shown (p. 11) that the temperature of $-273.2^{\circ} \text{ C.}$ is the lowest possible and represents an *absolute zero*. In scientific work, therefore, temperatures are often reckoned from this zero, the size of the degree being taken equal to that on the ordinary centigrade scale. In this way we get the *absolute scale of temperature*, in which negative numbers of degrees do not occur. Temperatures on the absolute and centigrade scales are connected by the equation

$$t^{\circ} \text{ abs.} = (t - 273.2)^{\circ} \text{ C.}$$

5. **Comparison of Mercury Thermometer with one containing some other Substance.**—The above measurement of temperature is based upon the *apparent*

* ANTOINE FERCHAULT SEIGNEUR DE RÉAUMUR (1683–1757), well known for his technical, botanical, and zoological work.

† JEAN ANDRÉ DELUC (born 1727 at Geneva, died 1817 at Windsor), Professor at Göttingen, lived mostly in London, Hanover, Berlin, and Brunswick.

‡ CELSIUS, born 1701, died 1744 at Upsala.

|| LINNÉ of the Botanical Garden at Upsala. In the preface of his *Hortus Upsaliensis*, written in 1748, he reports: "Greatest cold in the night of 1740 25 I, 28° below freezing-point, the freezing-point being designated by 0° and the boiling-point of water by 100° ." The Lyonese doctor LEON PIERRE CHRISTIN used a mercury thermometer with centigrade scale and introduced it into France. In Sweden, however, ELVIUS mentions a centigrade scale as early as 1710.

§ In England meteorological observations are still stated on the Fahrenheit scale. For other scientific purposes, however, the centigrade scale is always used.

(p. 9) volume expansion of mercury in glass. If we choose another substance (e.g. sulphuric acid), determine the fixed points and divide up the interval between them in the same manner, then the indication of the sulphuric acid thermometer so made will be slightly different from that of a mercury thermometer placed simultaneously in the same bath of water at an intermediate temperature. Thus for the same change of temperature the apparent expansion of the mercury is not proportional at all temperatures to that of the sulphuric acid. Hence if we wish to make a thermometer containing some other liquid than mercury, we must calibrate it from degree to degree against a correctly divided mercury thermometer. Besides mercury the only thermometric liquids in use are alcohol, petroleum ether, pentane, and toluene (see below).

6. Temperature of the Surroundings.—A mercury thermometer indicates directly only its own temperature. The fact that it also shows the temperature of the surroundings is due to the property of all bodies whereby their temperature changes until it becomes the same as that of their environment. Hence in determining a temperature the reading of the thermometer must not be taken until it has become constant.

7. Variations of the Fixed Points.—When a thermometer which indicates 0° C. correctly in melting ice is raised to a higher temperature (e.g. in boiling water) and then replaced in the ice, it will as a rule no longer indicate the correct temperature of 0° C. but a few tenths of a degree (up to 1° C.) lower. This *depression of the zero point* is due to an enlargement of the bulb. In the case of newly made instruments it is permanent and hence a new calibration is necessary. Even older thermometers which have been in long use show the same depression; in this case it is only temporary, however, and disappears after a short time.

If newly made thermometers be left out of use, i.e. exposed only to the variations of the air temperature, the bulb contracts slowly and causes a *secular* rise of the zero point*. In the course of years it may amount to several degrees.

The change of the zero point is dependent to a large extent upon the composition of the glass of which the thermometer is made. Instruments made of "Jena Normal Glass 16 III" bear a single longitudinal line of reddish-violet colour as trade mark; this guarantees a mean depression of not more than 0.05° C. The Jena glasses discovered later and known technically as "Borosilicate Thermometer Glass 59 III" and "Alkali-free Thermometer Glass 477 III" have the depression constants 0.035° C. and 0.014° C., the latter being the smallest yet attained. In order to avoid the *permanent* depression of the zero point in newly made thermometers and also to diminish the secular rise, the instruments are "artificially aged" by means of repeated rapid variations of temperature. Thermometers for scientific work should bear the name of the glass as well as a statement that they have been subjected to this treatment.

8. Calibration of a Thermometer.—The *zero point* is determined by placing the thermometer with the whole mercury thread under the surface of a mixture of distilled water and finely powdered ice free of salt. The thermometer must remain in the mixture until the mercury level no longer changes; this may take a considerable time, especially if the instrument has been previously subjected to a high temperature (see above). The final indication gives the zero point.

The upper fixed point, the boiling-point of water, is determined by placing the thermometer in the vapour from water boiling rapidly in a metal vessel or in a glass vessel containing pieces of metal (p. 67). The whole length of the mercury thread must be in the vapour and the bulb must not dip into the water but remain some distance above the surface. The vapour must be able to escape freely so that there is no excess pressure in the vessel. The mercury level must not be marked until sufficient time has elapsed for it to have become constant.

* Lat., *saeculum*, an age, a generation.

Even then it only gives the fixed point 100° C. when the atmospheric pressure is 760 mm. It has been found that the temperature t° C. indicated at barometric height b mm. is given by

$$t = 100 + 0.0375 (b - 760).$$

9. **Temperature and the Absolute System of Measurement.**—By means of the so-called laws of radiation (Vol. V) it is possible to refer temperature to the fundamental units of measurement, cm., gm., and sec. But it is not possible to determine the dimensions of temperature in this way, because the constants of these laws are not yet established with sufficient accuracy and it has not been decided what dimensions are to be associated with them. The product of the temperature T and a certain transformation constant k occurring in many laws (pp. 41 and 45) has the dimensions of energy, namely [dyne. cm.] = [gm. cm.² sec.⁻²]. If in accordance with the principles of the absolute measuring system this constant k were to be taken as of zero dimensions, then temperature would have the same dimensions as energy. This has not yet become customary, however, and consequently the dimension "degree" for temperature is regarded as independent of the fundamental dimensions of length (cm.), mass (gm.), and time (sec.). In this sense the constant k , for example, is regarded as having the dimensions erg/degree = [gm. cm.² sec.⁻² degree⁻¹].

10. **Thermodynamical Scale.**—Up to the present our definitions of temperature and the magnitude of a degree (p. 2) have been based upon the arbitrary choice of mercury as thermometric substance. In principle we might have made our definitions dependent upon any other substance. As has been seen above (p. 4), the temperatures would then have been different and the degrees of other magnitudes. It has therefore been the aim of physicists to arrive at a conception of temperature and a method of temperature measurement which are free from all arbitrariness, in particular independent of the particular properties of any chosen thermometric substance. One line of approach to this has already been mentioned, namely the laws of radiation. Another way, the one leading to the most exact and scientific definition of temperature which we have to-day, was pointed out as early as 1848 by WILLIAM THOMSON, afterwards LORD KELVIN (p. 124).

On the KELVIN scale the numerical value of any temperature is completely determined by the so-called second law of thermodynamics as soon as one point, say the lower fixed point, has been assigned some definite non-zero value T_0 . All other temperatures can then be evaluated by the measurement of certain definite processes, the so-called cycles (for further details see p. 111 *et seq.*). The scale defined in this way is known as the **thermodynamical scale of temperature**.

For all practical purposes it coincides very nearly with the temperature scale based upon the indications of a **gas thermometer** (for further information see p. 17). Indeed the thermodynamical scale would necessarily be identical with that of a thermometer filled with a perfect gas. Now the behaviour of real gases, especially hydrogen and helium, is almost ideal at low pressures. Hence the differences between the thermodynamical scale and the indications of a gas thermometer filled with a real gas (hydrogen or helium) at ordinary pressure can be determined and are known to-day with great accuracy. We are therefore enabled also to refer the indications of a mercury thermometer to the thermodynamical scale.

The following short table gives the differences between the thermodynamical and mercurial scales of temperature for two specified types of mercury thermometer.

Thermodynamical Temperature on the Centigrade Scale	Indication of a Mercury Thermometer made of Jena Glass, 16 III, with Equal Degree Divisions	Indication of a Mercury Thermometer made of Jena Glass, 59 III, with Equal Degree Divisions
-30°	-30.28°	-30.13°
-20	-20.16	-20.07
-10	-10.07	-10.03
0	0	0
+20	+20.09	+20.04
+50	+50.12	+50.03
+80	+80.06	+80.00
+90	+90.03	+89.98
+100	+100	+100
+200	+200.29	+200.84
+300	+302.7	+304.4

The differences are usually taken into account by the manufacturers of good thermometers, a correction to the thermodynamical scale being embodied by suitable deviations from equality in the degree markings.

11. **The Temperature Scale outside the Fixed Points.**—For the regions outside that between the melting-point of ice and the boiling-point of water a number of standard temperatures on the thermodynamical scale have been determined. Amongst these we may mention the following melting-points:

Mercury	-38.87°	Antimony	630.5°	Palladium	1549°
Tin	+231.85	Silver	960.5	Platinum	1755
Cadmium	320.9	Gold	1063	Tungsten	3400
Zinc	419.5	Copper	1083		

In addition there are the boiling-points of a number of substances at 760 mm. pressure, e.g. sulphur, 444.60°. Below -40° the standard temperatures are the boiling-points (at 760 mm. pressure) of carbon dioxide, -78.5°; oxygen, -183.0°; and hydrogen, -252.8°. Temperatures between these standard points are partly determined by the alteration of the electrical resistance (Vol. III) of platinum (from -193° to +630.5°), partly by the thermoelectric potential of a thermoelement (Vol. III) of platinum and 10 per cent rhodium-platinum (up to 1063°) and partly by the luminosity of a radiating black surface (above 1063°).

Liquid Thermometers for Low and High Temperatures.—Mercury thermometers cannot be used below -39° C. because mercury solidifies at this temperature. *Alcohol* or better *toluene* can be used down to -100° C. and *petroleum ether* or better *pentane* down to -180° C. On account of the markedly non-uniform expansion the length of the degree divisions of a liquid thermometer calibrated on the gas (thermodynamical) scale decreases at lower temperatures.

Liquid thermometers for high temperatures can be made by filling the space above the liquid with carbon dioxide or nitrogen under high pressure. Using high melting glass it is possible in this way to make mercury thermometers which can be used up to 600° C.; using silica (fused quartz) the range may even be extended up to 750° C. Since the gas pressure above the mercury is between 15 and 100 atmospheres, there is always a danger of explosion in using thermometers of this type.

2. Thermal Expansion of Solids

Linear Expansion.—When a solid body is heated the resulting increase of volume takes place in all directions. Most bodies (all isotropic bodies) expand in the same ratio in all directions simultaneously, but crystals sometimes expand differently in different directions (anisotropic). We will restrict our considerations to isotropic bodies. The expansion of a rod-shaped body in one direction (e.g. in the direction of its length) is called **linear expansion**.

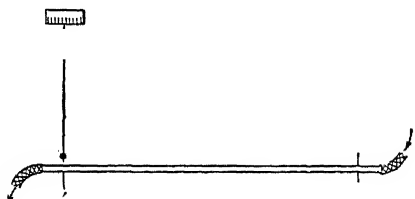


Fig. 2.—Measurement of Linear Thermal Expansion of a Metal Tube

An arrangement of the kind shown in fig. 2 may be used to measure the linear expansion of a solid. The substance to be investigated (e.g. brass) is taken in the form of a tube about 70 cm. long. Two notches are made upon this at a distance of 50 cm. apart. The tube is clamped at the first notch and rests with the other upon a horizontal knife-edge, which is fixed to a brass plate capable of rotation about a horizontal axis 5 mm. higher. The plate also carries a vertical pointer 25 cm. in length measured from the axis. Thus a small alteration in the length of the tube is magnified 50 times in transmission to the end of the pointer, where it can be read off upon a mirror scale. Rubber tubing is attached to the two ends of the tube so that a current of hot water or steam can be passed through it. The temperature of the water is read off upon mercury thermometers both as it enters and leaves the tube. When these readings are equal the tube has also taken up the same temperature.

The alteration in the length of the 50 cm. section of tube is noted when water at different temperatures is flowing through it. Observation shows that within the limits of error of the method the alteration of length is proportional to the alteration of temperature. Thus for each 1°C. rise in temperature the tube shows the same expansion. Now this expansion is obviously proportional to the original length of the tube. Hence we obtain a quantity independent of this length by dividing the linear expansion of the tube per degree by its original length. The quantity thus obtained is called the **coefficient of linear expansion** of the substance considered.

The coefficient of linear expansion of a solid is the ratio of its increase in length per 1°C. rise of temperature to its length at 0°C.

Its value for iron is 0.000012, for brass 0.000019, and for zinc 0.000029; for other substances see Table I (p. 289). For practical purposes the coefficients of linear expansion of substances in common use may be taken as constant at ordinary temperatures. This is in agreement with the result of the experiment described above, namely that the change of length is proportional to the change of temperature. Letting α be the coefficient of linear expansion, a rod of length l will expand by an amount $l\alpha$ for 1°C. rise of temperature and by an amount $l\alpha t$ for $t^{\circ}\text{C.}$ rise of temperature. The new length will then be $l + l\alpha t$. If l_0 be the length of the rod at 0°C. and l_t the length at $t^{\circ}\text{C.}$, we have therefore

$$l_t = l_0(1 + \alpha t).$$

Accurate observations have proved that the expansion per 1° C. is not independent of the initial temperature, i.e. that the coefficient of linear expansion is not a constant. If it is desired to take this into account, it is necessary to state within which temperature range or from what initial temperature the expansion has been measured.

Compensated Pendulum.*—This is a pendulum in which the increase of length due to rise of temperature is neutralized by the use of a suitable combination of different metals. The pendulum rod (fig. 3) consists of three rods of iron and two of zinc arranged in the manner depicted (*gridiron pendulum*). As a result of the thermal expansion of the iron rods the pendulum increases in length with rise of temperature; but as a result of the expansion of the zinc rods the top of the middle iron rod is raised to such an extent that on the whole the pendulum length remains constant at all temperatures.



Fig. 3.—
Compensated
(Gridiron)
Pendulum

Such compensated pendulums were much used formerly in accurate clocks. In more modern times it has been possible to make a metallic alloy (steel with about 36 per cent nickel) called *invar*† whose coefficient of linear expansion is so small as to be practically negligible. In modern accurate clocks use is made of this alloy and the pendulums are constructed with a simple rod.

Metallic Thermometer.—This consists of two strips of metal of different coefficients of expansion (e.g. iron and brass) riveted together

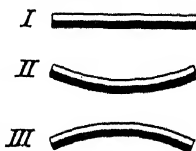


Fig. 4.—Bimetallic Strip

firmly (so-called bimetallic strip, fig. 4). If the strip is straight at some intermediate temperature (e.g. 20° C.), it will become curved with rise of temperature so that the brass is on the convex side, and with fall of temperature so that the brass is on the concave side; for the brass has the greater coefficient of expansion and therefore expands more than the iron when the temperature is raised and contracts more when the temperature is lowered. In order to accommodate a long strip in a small space, it is often coiled round into the form of a spiral, the middle of which is held fixed while the outer end carries a pointer. The motion of the end of the pointer is generally registered by means of a coloured pencil or pen (thermograph; for figure see Vol. V).

Cubical Expansion.—In the case of an isotropic body the linear expansion is the same in all directions. Hence the shape remains similar when the temperature is altered. Now the volumes of similar bodies are in the ratio of the cubes of corresponding linear dimensions and hence we have the equation

$$V_t : V_0 = l_t^3 : l_0^3 = l_0^3(1 + at)^3 : l_0^3,$$

whence

$$V_t = V_0(1 + at)^3 = V_0(1 + 3at + 3a^2t^2 + a^3t^3).$$

Since the coefficient of linear expansion a is a very small quantity, we can neglect

* The compensated pendulum as a regulator for accurate clocks was discovered by JOHN HARRISON (1693–1776), who was originally a carpenter. He received a prize of £5000 for it from Parliament in 1758 and another prize of £10,000 in 1765 for improvements to his clocks (ship's chronometers). It is possible that GEORGE GRAHAM (1675–1751), an excellent mechanic and clockmaker, was acquainted with the compensated pendulum before HARRISON. GRAHAM attempted to obtain the same result later with a pendulum whose bob consisted of a vessel containing mercury.

† From "invariable".

the terms of second and third degree in a in comparison with the term of the first degree. The equation then simplifies to

$$V_t = V_0(1 + 3at).$$

The quantity $3a$ is called the **coefficient of cubical expansion**.

The coefficient of cubical expansion of a substance is equal to three times the coefficient of linear expansion.

3. Thermal Expansion of Liquids

Since liquids and gases have no definite shape we only have to consider their coefficients of *cubical* expansion. Now a liquid must always be enclosed in a vessel, which will also increase in volume with rise of temperature. Hence it is only possible to observe the *apparent* expansion of the liquid in the vessel. In order to obtain the coefficient of *true* or *absolute* expansion account must also be taken of the expansion of the vessel.

The measurement is usually carried out in the following way: A pyknometer (Vol. I) is completely filled with mercury and weighed. It is then heated in a water bath to a known temperature. A certain amount of mercury flows out of the pyknometer and its volume is determined by weighing again, subtracting from the original weight and dividing the difference by the specific gravity of mercury. The volume expansion so measured is the apparent expansion, i.e. the difference between the expansion of the mercury and that of the glass. Thus to get the absolute expansion we have to add the increase of volume of the vessel as calculated from the equation $V_t = V_0(1 + 3at)$ on pp. 8, 9, knowing the value of a , the coefficient of linear expansion of the glass. The true expansion of the mercury, corrected in this way, is then divided by the rise of temperature and by the original volume. This gives the value 0.00018 for the coefficient of absolute (cubical) expansion of mercury.

With the help of the theorem that the heights of the liquid columns in communicating vessels are inversely proportional to their respective specific gravities (Vol. I), it is possible to determine the coefficient of absolute expansion of a liquid by the following direct method. The vertical limbs of a U-tube (fig. 5) are surrounded by jackets through which water is passed at different temperatures. In this way a known difference of temperature is maintained between the liquid columns in the two limbs. If the U-tube is filled, for example, with mercury, the specific gravity of the mercury in the hotter limb is smaller than in the colder limb, and consequently the level in the hotter limb is higher. The ratio of the lengths of the two liquid columns is measured; this is the same thing as the ratio of the volumes of a given mass of liquid at the respective temperatures of the water jackets (method of DULONG and PETIT).

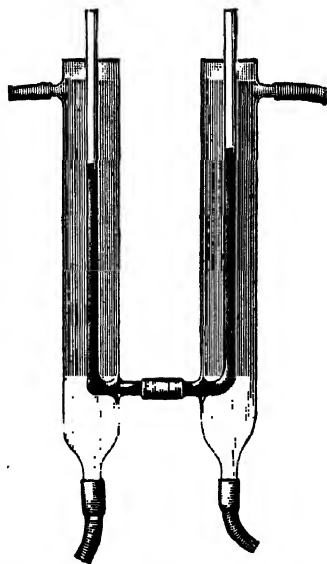


Fig. 5.—Measurement of the Thermal Expansion of a Liquid

The coefficient of expansion of most liquids is different in different temperature ranges. Hence it is necessary always to state over which temperature range it has been measured. Table I (p. 289) gives the values for some liquids at 18°C .

Expansion of Water.—The change in magnitude of the coefficient of expansion of water at different temperatures is particularly remarkable.

This shows itself clearly if we make a thermometer containing water and place it along with a mercury thermometer in a water bath which is gradually warmed up. In this experiment only the apparent expansion of the water is visible (on account of the simultaneous expansion of the glass containing it) and therefore we introduce the following modification. Inside the water thermometer we enclose a body which expands with rise of temperature to such an extent as just to compensate the increase in volume of the thermometer due to

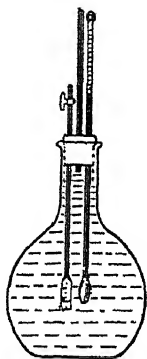


Fig. 6.—Measurement of the Thermal Expansion of Water

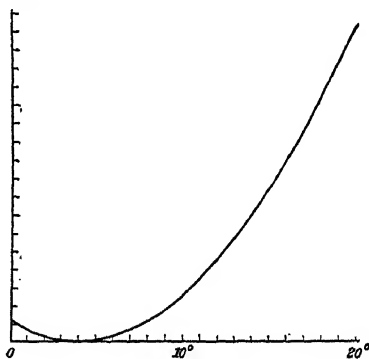


Fig. 7.—Expansion of Water with Rise of Temperature. (Ordinates: 1 div. = 0.0001 of vol. at 4°C .)

the expansion of the glass. We shall learn below that the coefficient of expansion of air is 0.00367. The coefficient of cubical expansion of glass is 0.000021, i.e. 175 times smaller than that of air. If therefore we enclose an air bubble of volume 2 cm^3 in a flask of volume 350 cm^3 , the expansion of the vessel will be just neutralized by that of the bubble (fig. 6). We also furnish the flask with a narrow glass tube open at the top and a mercury thermometer, both passing through a tight stopper. When now the apparatus is warmed up slowly in a water bath, the temperature can be read off on the mercury thermometer and the volume change of the water on the narrow open tube. We plot the temperatures as abscissæ and the corresponding water levels as ordinates, and thus obtain the curve shown in fig. 7.

At 4°C the volume of the water is a minimum. When heated uniformly from 0°C ., the volume first decreases slowly to 4°C ., then begins to increase, reaches approximately its original value at 8°C ., and thereafter goes on increasing more and more rapidly. In Table II (p. 290) are given the volumes at each successive degree between 0°C ., and 20°C ., the volume at 4°C ., being put equal to unity. For higher temperatures see p. 158, fig. 27.

Since a given mass of water has its minimum volume at 4°C ., the density must also be a maximum at this point. This is the reason why the temperature of the water at the bottom of a tall vessel cooled at the top (e.g. by addition of pieces of ice) only falls to 4°C . As long as the surface water is at a temperature above 4°C . it becomes heavier when cooled and sinks to the bottom; but below 4°C . it becomes lighter when cooled and hence remains at the top. For the same reason deep waters never freeze at the bottom; the ice layer forms at the surface.

4. Thermal Expansion of Gases. Absolute Temperature

1. **Coefficient of Expansion.**—To measure the (cubical) expansion of gases, use may be made of a spherical glass bulb (fig. 8) of about 100 cm.^3 capacity on

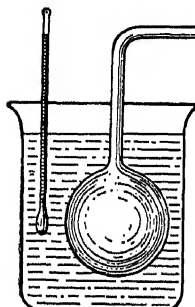


Fig. 8.—Thermal Expansion of Gases

the end of a narrow tube bent at right angles and having its longer limb horizontal (see figure). The bore of the tube is determined by previous experiment. The bulb is filled with dry air, which is enclosed by a drop of liquid placed in the horizontal part of the tube to serve as index. The bulb is placed in a water bath, whose temperature can be read off by means of a mercury thermometer and the position of the index noted. If now the temperature of the bath and hence also of the air in the bulb (*dilatometer*) is raised, the increase of volume can be observed and measured from the movement of the index along the tube of known bore.

Suppose that the volume of the air enclosed by the index at 0°C . is 100 cm.^3 . When the bath is heated up we observe that the index moves along proportionally to the temperature. Measurements of this kind have given the value $\alpha = 0.00367 = 1/273$ for the coefficient of cubical expansion (**volume coefficient**) in the equation $V_t = V_0(1 + \alpha t)$ (p. 8). If we fill the dilatometer with other gases we always obtain the *same* coefficient of expansion. This is known as **Gay-Lussac's law**.*

The coefficient of thermal expansion (volume coefficient) is almost exactly the same for all gases, the mean value being

$$\alpha = 1/273.2 = 0.0036604.$$

This is the value for an ideal or perfect gas (p. 14). Actual measure-

* This law, wrongly named after GAY-LUSSAC, was first proved by the Parisian scholar AMONTONS (1663–1705). AMONTONS invented the air thermometer. He was also of the opinion that heat consisted of a lively motion of small heat particles which could be transferred to the particles of the body: the higher the temperature, the greater the velocity of these heat particles and of the material particles set in motion by them. On this theory AMONTONS calculated the temperature at which the material particles would have no motion at all and obtained the value -239.5°C . According to more accurate measurements this temperature, which is to-day called the *absolute zero*, is -273.2°C .

ments, which can only be carried out with real gases, have given the following figures:

for helium, $\alpha = 0.0036604 - 0.0000019 p_0$;

for hydrogen, $\alpha = 0.0036604 - 0.0000012 p_0$;

for nitrogen, $\alpha = 0.0036604 + 0.0000127 p_0$;

where p_0 is the pressure of the gas at 0° C. expressed in metres of mercury.

2. Pressure Coefficient.—In the above apparatus (fig. 8) it was assumed that the liquid drop serving as index could move easily, so that the gas was able to expand at a constant pressure equal to that of the atmosphere. We will now modify the experiment by connecting the dilatometer to an open mercury manometer (fig. 9). The tube from the bulb and also that of the manometer must be so narrow that the change of volume corresponding to the alteration of the mercury level in the manometer can be neglected. When the air in the dilatometer is heated, the difference of level in the two limbs of the manometer increases, i.e. the pressure of the air increases at constant volume, being equal to atmospheric pressure plus that indicated by the difference of the mercury levels. The observed increase of pressure is found to be proportional to the rise of temperature.

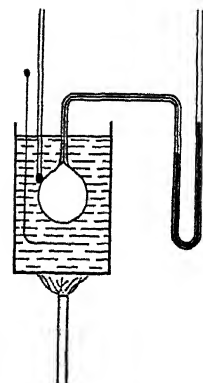


Fig. 9.—Measurement of the Pressure Coefficient of a Gas

If p_0 be the pressure of the air at 0° C., and p_t that at t° C., then

$$p_t = p_0(1 + \beta t), \text{ where } \beta = 0.0036604 = 1/273.2.$$

The quantity β is called the **pressure coefficient**; except for slight deviations its value is the same for all gases and practically equal to the volume coefficient. The following are the values actually found:

for helium, $\beta = 0.0036604 - 0.0000004 p_0$;

for hydrogen, $\beta = 0.0036604 + 0.0000017 p_0$;

for nitrogen, $\beta = 0.0036604 + 0.0000134 p_0$;

where p_0 is the pressure of the gas at 0° C. expressed in metres of mercury. For vanishingly small pressures ($p_0 = 0$) both the *volume coefficient* α and the *pressure coefficient* β approach the same limiting value $\gamma = 0.0036604$.

3. The Boyle-Gay-Lussac Law.—At constant temperatures the volume and pressure of a given mass of gas are connected by Boyle's law, viz.

$$pV = \text{const.}$$

A change of temperature can cause changes both of pressure and of volume. But, as in the above experiments, one or other of these quantities may be kept constant. In order to arrive at a general relationship between the volume, pressure and temperature of a given mass of gas, we first consider the temperature to be raised from 0° C. (at which the volume is V_0 and the pressure p_0) to t° C. Then according to Gay-Lussac's law the new volume V_t is given by the equation

$$V_t = V_0(1 + \alpha t).$$

We now keep the gas at the constant temperature t° C. and change its volume V_t and pressure p_0 to the values V and p respectively. Then by Boyle's law

$$pV = p_0V_t,$$

and hence

$$pV = p_0V_t = p_0V_0(1 + \alpha t).$$

We can also carry out the changes by keeping the volume V_0 constant as the temperature is raised from 0° C. to t° C. In this case the new pressure p_t is determined by Gay-Lussac's law, viz.

$$p_t = p_0(1 + \beta t). \quad . \quad . \quad . \quad . \quad . \quad (1)$$

We now produce a simultaneous change of the volume V_0 and pressure p_t to the values V and p respectively, keeping the temperature t° C. constant. The product of pressure and volume must once more remain constant by Boyle's law, and we must have the equation

$$pV = p_tV_0 = p_0V_0(1 + \beta t). \quad . \quad . \quad . \quad . \quad . \quad (2)$$

This is not only similar to equation (1) in form; the two are identical, since the quantity α (the coefficient of thermal expansion) in equation (1) is equal to the quantity β (the coefficient of thermal increase of pressure) in equation (2). Hence we can express the relationship between the volume, pressure, and temperature of a given mass of gas quite generally by means of the equation

$$pV = p_0V_0(1 + \alpha t).$$

This is called the **Boyle-Gay-Lussac law**. At constant temperature the equation becomes identical with that of Boyle's law; at constant pressure or volume (and variable temperature) it assumes the form of the equation expressing Gay-Lussac's law.

4. **Absolute Temperature** (see p. 11, footnote).—We transform the last equation by substituting $\alpha = 1/273.2$ and get

$$p_tV_t = p_0V_0\left(1 + \frac{t}{273.2}\right) = p_0V_0\left(\frac{273.2 + t}{273.2}\right).$$

By putting $273.2 + t = T$ we introduce a temperature T corresponding to $t^\circ \text{C.}$ but referred to a zero point lying 273.2°C. below the temperature of melting ice (0°C.). This zero point is called the **absolute zero** and temperature measured from it in centigrade degrees is called the **absolute temperature**. Thus the melting-point of ice is $T_0 = 273.2^\circ \text{abs.}$ * on this scale.

5. Equation of State.—Making use of the concept of absolute temperature, the last equation simplifies to

$$\frac{p_t V_t}{T} = \frac{p_0 V_0}{T_0} = \text{const.}$$

This equation is called the **equation of state** of the mass of gas considered. It is also known as the **Boyle - Gay-Lussac law** and can be expressed in words as follows:

For a given mass of gas the product of the pressure and volume divided by the absolute temperature is a constant.

The absolute zero and absolute temperature are concepts which greatly facilitate the mathematical expression and application of the Boyle-Gay-Lussac law. We know nothing about the state or the behaviour of bodies at the absolute zero, because, though it has been possible to come very near to it, this temperature has never yet been reached. If we were to apply the Boyle-Gay-Lussac law at the lowest temperatures, we should be led to the meaningless equation $p_0 V_0 = 0$, from which we should deduce that a gas at the absolute zero would either have no volume or would exert no pressure. We know, however, that *all* gases sooner or later become liquid when cooled, so that at the temperature of the absolute zero the gaseous state probably no longer exists.

The Boyle-Gay-Lussac law is only an approximation (p. 90; Vol. I, p. 315). The farther the state of a gas from the point at which it liquefies (p. 88), the more nearly it obeys the Boyle-Gay-Lussac law. Only for an ideal or perfect gas would the law hold strictly. The smaller the density of a real gas becomes with decrease of pressure, the more nearly its behaviour approaches that of a perfect gas and the better it obeys the law.

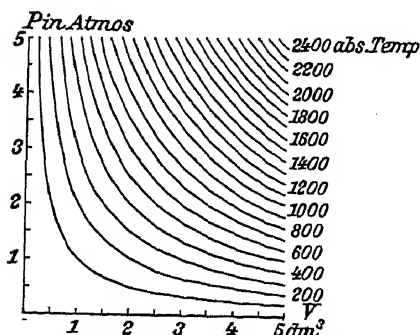


Fig. 10.—Pressure-Volume Isotherms

means of a system of curves obtained by plotting $pV/T = \text{const.}$ for a number of different temperatures, say $T = 100^\circ, 200^\circ, 300^\circ \text{abs.}$, &c.

In fig. 10 it has been assumed that a certain mass of gas has the

* Instead of $T^\circ \text{abs.}$ it has recently become usual in certain sections of physical literature to write $T^\circ \text{K}$ (read “degrees Kelvin”, see p. 5).

6. Gas Isotherms.—We can represent the essential content of the Boyle-Gay-Lussac law by

volume $V = 1$ litre at the temperature $T = 100^\circ$ abs. and the pressure $p = 1$ atm. We plot the curve of $pV = 1$, taking the volumes as abscissæ and the corresponding pressures as ordinates. Since this curve applies for a constant temperature of $T = 100^\circ$ abs., it is called an **isothermal curve** or **isotherm*** for this temperature. The isotherm for 200° is derived from the equation $pV = 2$, that for 300° from $pV = 3$, &c.

We can read off at once from the diagram what volume the chosen mass of gas will have at any temperature and pressure. Thus, for example, at $T = 600^\circ$ abs. and $p = 2$ atm. the volume is $V = 3$ dm.³, for the ordinate $p = 2$ corresponds on the isotherm for $T = 600^\circ$ abs. to a point at which $V = 3$.

7. The Perfect Gas.—A gas obeying the above equations exactly is called an **ideal** or **perfect gas**. Real gases of simple constitution may be regarded as approximately perfect at low pressures. At higher pressures deviations occur (p. 90); these are due to the increased importance of molecular forces.

8. Specific Gas Constant.—The value of the expression $p_0 V_0 / T_0$ depends only upon the nature and the quantity of the gas in question. It is usual to consider 1 gm. of the gas and to express the pressure in dynes per square centimetre and the volume in cubic centimetres. Now 1 gm. of air under normal conditions of temperature and pressure occupies a volume $V_0 = 1/0.001293 = 1000/1.293$ cm.³, and the pressure of a column of mercury 760 mm. long is equal to $p_0 = 1033.981$ dynes/cm.². Hence for 1 gm. of air

$$\frac{p_0 V_0}{T_0} = \frac{1033.981 \cdot 1000}{1.293 \cdot 273} = 2.871 \cdot 10^6 \text{ ergs/degree.}$$

In the same way we obtain for oxygen the value $2.597 \cdot 10^6$, for nitrogen $2.967 \cdot 10^6$ and for hydrogen $41.25 \cdot 10^6$. These are called the **specific gas constants** of the different gases. Using the value for hydrogen, for example, we obtain for m gm. of this gas

$$\frac{pV}{T} = 41.25 m \cdot 10^6.$$

9. Universal Gas Constant.—The last equation assumes a particularly simple form if we consider a quantity of gas whose mass in grammes is numerically equal to its molecular weight. This quantity is called a **gramme-molecule** or a **mol**. If the molecular weight of the gas is μ , then the quantity of mass μ gm. is a mol. Thus, for example, one mol. of oxygen is 32 gm., one mol. of nitrogen is 28.02 gm., one mol. of hydrogen 2.016 gm., and so on.

If for each gas we multiply the specific gas constant by the molecular

* Gr., *isos*, equal; *thermós*, hot.

weight, we get for oxygen $32.2597 \cdot 10^6 = 8.312 \cdot 10^7$, for nitrogen $8.314 \cdot 10^7$, and for hydrogen $8.316 \cdot 10^7$, i.e. the same value in each case. The most accurate numerical value is taken as $8.313 \cdot 10^7$. This is known as the **universal gas constant** and is denoted by R . Thus for 1 mol of a gas the equation of state simplifies to

$$\frac{pV}{T} = R = 8.313 \cdot 10^7.$$

10. The Clapeyron Equation of State.—If we wish to apply the above equation to an arbitrary quantity of gas, we must know the number ν of mols it contains. We can then write the equation in the form

$$\frac{pV}{T} = R\nu, \quad R = 8.313 \cdot 10^7 \left[\frac{\text{Erg}}{\text{Degree} \cdot \text{Mol}} \right].$$

This is known as the **CLAPEYRON*** equation of state for gases.

11. Molar Volume.—With the help of the Clapeyron equation of state we can calculate the volume V_0 of one mol of a gas at *normal temperature and pressure* (N.T.P.) by putting $p_0 = 1033.981$ dynes per cm^2 and $T = 273.2$. Then

$$V_0 = \frac{8.313 \cdot 10^7 \cdot 273.2}{1033.981} = 2.241 \cdot 10^4 \text{ cm}^3 = 22.41 \text{ litres}.$$

We can also calculate this value directly by dividing the molecular weight 2.016 of hydrogen by the known weight of 1 litre of the gas at N.T.P. We get

$$\text{molar volume} = V_0 = 2.016/0.09 = 22.4 \text{ litres}.$$

12. Avogadro's Law.—The fact that the molar volume of all gases is the same has been explained by assuming that the number of molecules in a given volume is the same for all gases under the same conditions (see p. 53).

This hypothesis was first made by **AVOGADRO**† in 1811, who was led to it from considerations of the behaviour of gases in chemical reactions. Since its experimental verification it is known as **Avogadro's law**, and is usually expressed as follows:

At the same temperature and the same pressure equal volumes of different gases contain equal numbers of molecules.

From this it follows further that:

The densities of two gases are in the same ratio as their molecular weights.

* **B. P. E. CLAPEYRON** (1799–1864), French engineer.

† **COUNT AMADEO AVOGADRO DI QUAREGNA DI CERETTO**, born 1776 at Turin, died 1856, was first a jurist, then devoted himself to natural science and obtained in 1820 the chair of mathematical physics at Turin, which he occupied intermittently until 1851.

13. Dissociation.—Let n be the number of molecules in 1 gm. of hydrogen and d the density of a gas relative to hydrogen at the same temperature and pressure. Then the number of molecules in 1 gm. of the gas is given by the quotient n/d . Hydrogen obeys the laws of Boyle and Gay-Lussac almost perfectly. For all gases which also obey these laws d must remain constant when the temperature is altered, and consequently the number of molecules contained in a mass of 1 gm. must also remain constant. If now the density of such a gas relative to hydrogen at the same temperature and pressure changes with temperature (as, for example, in the case of N_2O_4 , where d becomes smaller with rise of temperature), it follows that the number of molecules per gm. must also have changed. The simplest explanation of this phenomenon is obtained by assuming that the complex molecules of such gases decompose with rise of temperature, so that each molecule gives rise to two or three. This process is called gaseous **dissociation** (compare p. 80).

5. Gas Thermometers

In § 1, p. 2 *et seq.*, we based the definition of the centigrade scale upon the expansion of mercury. If the coefficient of expansion of gases were proportional at all temperatures to that of mercury, the indications of a gas thermometer would coincide at all temperatures with those of a mercury thermometer. This is only approximately the case, however.

A mercury thermometer which is not gas-filled can at most only be used between the freezing-point and boiling-point of mercury, i.e. between about -40° C. and $+357^\circ$ C. It is therefore desirable to have a thermometric substance which can be used at all temperatures. For this reason a second scale of temperature has been set up; it is based upon the correctness of the Boyle-Gay-Lussac law.

The farther the state of a gas from its liquefaction point, i.e. the higher its temperature and the lower its pressure, the better it obeys this law. In laying down an "international legal measure of temperature" in 1887 the International Committee for weights and measures took the behaviour of hydrogen as basis, because it obeyed the Boyle-Gay-Lussac law the best of all the then known gases. It was not found till later that helium has a still lower liquefaction-point than hydrogen. Hydrogen becomes liquid at -252.8° C., helium at -268.71° C.

The instruction of the International Committee of Weights and Measures in 1887 was:

Temperature shall be measured by the gaseous pressure of a constant volume of chemically pure hydrogen, which at the melting-point of ice exerts a pressure equal to that of a mercury column 1000 mm. in length. The fixed points of the thermometer shall coincide with those of the Celsius scale.

The value of the pressure coefficient, (p. 12) of hydrogen is taken as $\beta = 0.0036621$.

The *thermodynamical scale* differs only very slightly from that of a hydrogen or nitrogen thermometer; see the following table.

Thermo- dynamical Scale	Constant Volume		Constant Pressure	
	Hydrogen	Nitrogen (or Air)	Hydrogen	Nitrogen (or Air)
-200°	+0.07°	+0.52°	+0.25°	+5.42°
-100	0.02	0.05	0.02	0.46
0	0	0	0	0
+50	0.000	-0.009	-0.001	-0.024
100	0	0	0	0
200	+0.003	+0.046	+0.005	+0.11
500	0.02	0.280	—	0.65
1000	0.05	0.77	0.07	1.65

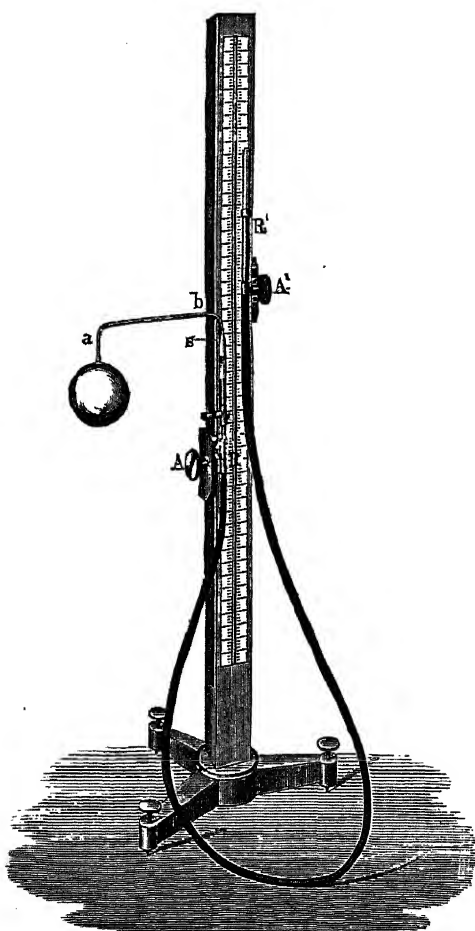


Fig. 11.—Jolly's Constant-volume Air Thermometer

Jolly's * Air Thermometer.—Measurement of temperature with the air thermometer necessitates the simultaneous observation of volume and pressure. The apparatus is therefore arranged so that the volume of the enclosed air remains constant.

A practical form of constant-volume air thermometer, suggested by JOLLY in 1874, is shown in fig. 11. A glass globe *a* filled with dry air is connected by means of a fine capillary *b* with a wide glass tube whose lower end is connected by thick-walled rubber tubing with a tube capable of movement along a scale. The two tubes joined with the rubber tubing contain mercury. Close below the end of the capillary is a mark *s* determined by a fine point of glass. The globe is surrounded with a mixture of water and ice, whereby it is brought to the temperature $T_0 = 273.2^\circ$ abs., and the movable tube is then raised until the mercury surface just touches the glass point *s*. The difference in the mercury levels in the two tubes (from *s* to *R'*) plus the atmo-

spheric pressure as read off from a barometer gives the pressure p_0 . Hence all the quantities in the expression $p_0 V_0 / T_0$ are known except V_0 .

* G. PH. VON JOLLY (1809-84), Professor of Physics at Munich.

If then the globe of the air thermometer is dipped into the liquid whose temperature is to be measured (which we will suppose to be higher than that of melting ice), the movable tube will have to be raised farther in order to bring the mercury surface back into contact with the point *s*. In the new expression $p_1 V_1 / T_1$ we know the pressure p_1 (sum of atmospheric pressure and observed difference of mercury levels), and since $V_1 = V_0$ we get by the BOYLE-GAY-LUSSAC law the equation

$$\frac{p_1 V_0}{T_1} = \frac{p_0 V_0}{T_0}.$$

Here V_0 cancels on both sides and we have

$$T_1 = 273 \cdot 2 p_1 / p_0.$$

In measurements with the air thermometer it is usual to neglect the expansion of the glass, since this is 175 times smaller than that of the air. For this reason also the inconveniences of zero point variation due to after effects in the glass (p. 4) do not arise. If a globe of silica be used, there is no need to take its change of volume into account even in the most accurate work; for the coefficient of expansion of silica is less than a tenth of that of glass.

Air Thermoscope.—The large thermal expansion of gases has led to the construction of simple thermoscopes with which it is possible to demonstrate changes of temperature to a large audience. Such thermoscopes consist of an air container connected by means of rubber tubing to an open liquid manometer.

Geometrical or Dalton Scale of Temperature.—The measurement of temperature and therewith the conception of temperature as a measure of thermal state is based upon the expansion of certain specially selected substances. The thermodynamical scale (p. 5), which defines temperature in a satisfactory scientific manner, also makes use of a substance, namely a perfect gas. It is a common postulate of both these definitions that equal increases of volume of the thermometric substance shall correspond to equal increases of temperature. This is, of course, purely arbitrary. In principle it would have been equally justifiable to postulate that equal *relative* increases of volume of a perfect gas should correspond to equal rises of temperature. We should then have arrived at a temperature scale differing considerably from the usual one. Such a scale was proposed by DALTON* in 1802. If t is the centigrade temperature and τ the corresponding temperature on the Dalton scale, then provided that the two coincide at 0° and 100° ,

$$t = 273 \left[\left(\frac{373}{273} \right)^{\tau/100} - 1 \right].$$

Hence when $t = -273$, $\tau = -\infty$.

If the geometrical scale were used instead of the ordinary one, the concept of an absolute zero would be avoided. The temperature range of 1° C. between $-272 \cdot 2^\circ$ C. and $-273 \cdot 2^\circ$ C. would correspond to an infinitely large temperature range on the Dalton scale. This teaches us therefore that the *concept of an absolute zero arises only from the customary definition of temperature and the behaviour of a perfect gas; it can be avoided by a modified method of reckoning temperature.* Most of the natural laws would, however, assume a much less simple form if the temperature were measured on the Dalton scale instead of on the customary one.

* JOHN DALTON (1766–1844), English scientist, particularly famous for his discovery of the law of multiple proportions in chemistry and his explanation of it in terms of atoms, through which he became the originator of the atomic theory of chemical processes. He also discovered colour blindness in himself (green-red blindness—daltonism).

6. Quantity of Heat. Specific Heat

1. **Quantity of Heat.**—A beaker containing 1 kg. of water is heated over a gas flame and the temperature read off on a thermometer. In 5 min. a rise of about 20°C. is observed. Then $\frac{1}{2}$ kg. of water is placed in a beaker of the same size and the experiment repeated. The rise of temperature in 5 min. is now about 40°C. In the same time the same source of heat now causes twice the rise of temperature noted in the first case. The product of the mass of the water and the rise of temperature remains constant; hence we can look upon it as a measure of the thermal effect of the flame. It is called a *quantity of*

The unit quantity of heat is that required to raise the temperature of 1 kg. of water from $14\frac{1}{2}^{\circ}\text{C.}$ to $15\frac{1}{2}^{\circ}\text{C.}$

It is known as the **kilogram-calorie*** or large calorie (abbreviated kcal. or Cal.). The **gramme-calorie** or small calorie (abbreviated cal.) is also used as a smaller unit; it is the quantity of heat required to raise the temperature of 1 gm. of water from $14\frac{1}{2}^{\circ}\text{C.}$ to $15\frac{1}{2}^{\circ}\text{C.}$ †

Assuming that the quantity of heat required to raise the temperature of a certain mass m of water from $\theta^{\circ}\text{C.}$ to $(\theta + 1)^{\circ}\text{C.}$ is independent of the initial temperature, we can calculate the quantity of heat Q from the rise of temperature t by means of the equation

$$Q = mt.$$

For accurate measurements the quantity of heat required to raise the temperature by 1°C. must be specially determined from degree to degree; for in reality it is not exactly the same in all temperature ranges. The deviations are so small, however, that they may be neglected for our purposes.

2. **Specific Heat.**—We modify the experiment described above by placing first a spiral of lead wire weighing $\frac{1}{2}$ kg. in the beaker and then adding $\frac{1}{2}$ kg. of water. The total mass is thus 1 kg. as before. We heat the beaker and contents with the same flame as in the previous experiment and observe after 5 min. a rise of temperature of about 38.8°C. From this it follows that $\frac{1}{2}$ kg. lead does not require as much heat as $\frac{1}{2}$ kg. water in order to raise its temperature by 1°C. ‡

In the first experiment the flame heated up 1 kg. of water by 20°C. in 5 min.; it therefore furnished 20 Cal. In the last experiment the same flame must have furnished the same quantity of heat. Since now $\frac{1}{2}$ kg. water was heated up by 38.8°C. , the quantity of heat given

* Lat., *calor*, heat.

† The kilogram-calorie (15°C. -kilogram-calorie) is the official unit. It is equal to the *mean kilogram-calorie* measured between 0°C. and 100°C. , and is 1.008 times the *RÉGNAULT* 0°C. -kilogram-calorie, i.e. the quantity of heat required to raise the temperature of 1 kg. of water from 0°C. to 1°C.

‡ In this experiment we neglect the quantity of heat given up by the flame to the vessel and the air.

up to the water was $38.8 \cdot \frac{1}{2} = 19.4$ Cal. Therefore the quantity required to raise the temperature of $\frac{1}{2}$ kg. of lead by 38.8° C. was only 0.6 Cal. Hence 1.2 Cal. would be necessary to raise the temperature of 1 kg. of lead by 38.8° C. or $1.2/38.8 = 0.03$ Cal. to raise the temperature of 1 kg. of lead by 1° C.

If we repeat the same experiment with other substances, we find a different rise of temperature in each case; but it is always smaller than when we heat $\frac{1}{2}$ kg. of pure water alone. It follows therefore that unit mass of every substance requires a definite positive quantity of heat (*the specific heat*) to raise its temperature by 1° C. This quantity depends upon the nature of the substance.

The specific heat of a substance is the quantity of heat necessary to raise the temperature of 1 gm. of the substance by 1° C.

The quantity of heat is expressed here in gramme-calories. If 1 kg. be chosen as the unit of mass, then the quantity of heat must be expressed in kilogram-calories. The specific heat of a body is not the same at all temperatures (p. 25), and hence for accurate calculations it is necessary to state at what temperature the determination has been carried out.

3. Heat Capacity.—If c be the specific heat of a body and m its mass in gm., the quantity of heat (expressed in gramme-calories) required to raise its temperature by 1° C. is

$$K = mc.$$

This is called the **water equivalent** or **heat capacity** of the body. Since for water $c = 1$, K is numerically equal to that mass of water requiring the same quantity of heat to raise its temperature by the same amount. To heat up the body by t° C. the quantity of heat required will be

$$Q = mct = Kt.$$

4. Historical.—The concept of quantity of heat was probably first formulated clearly by GEORGE WILHELM RICHMANN (1711–55, member of the Petersburg Academy). Specific heat was introduced after 1762 by JOSEPH BLACK (1728–99, from 1756 Professor of Chemistry in Glasgow, and from 1766 in Edinburgh). JOHANNES KARL WILCKE (born 1732 at Weimar, died 1796 as Secretary of the Academy of Stockholm) determined the first specific heats about 1772.

7. Determination of Specific Heats

1. Calorimetry.—The measurement of heat is called *calorimetry*; the apparatus used is called a *calorimeter*. Most accurate determinations of specific heat are made by this method.

I. Determination of the Specific Heat of a Solid. Metal Calorimeters.—In principle the simplest method of determining specific heat is to add a measured quantity of heat to a weighed amount of the substance and to determine the rise of temperature. The most important point here—as indeed in all calorimetric measurements—is to prevent losses of heat to the surroundings. Measurements of this kind can be performed in a very simple and straightforward

manner in a **vacuum calorimeter** (NERNST), a piece of apparatus especially suitable for measurements at low temperatures.

A massive block of the substance to be investigated is heated electrically in an evacuated vessel (fig. 12) surrounded by a bath at the desired temperature (e.g. that of liquid air). The quantity of heat added is determined from the easily measured quantity of electrical energy used (Vol. III), and the temperature of the body is determined from the electrical resistance of the heating wire, which varies with temperature (Vol. III). The evacuation of the calorimeter considerably reduces loss of heat to the surroundings (p. 178).

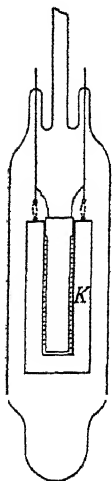


Fig. 12.—
Nernst Vacuum
Calorimeter

A hollow copper block (of about $\frac{1}{2}$ kg. wt. and known heat capacity) electrically heated in a vacuum can also be used to contain the body under investigation (copper calorimeter of Nernst).

The Method of Mixture.—In a thin-walled vessel K (fig. 13) (the calorimeter) is placed a known quantity of water whose temperature is read off on a thermometer marked in tenths of a degree. The body to be investigated (e.g. small pieces of metal) is heated up to an accurately known temperature in a test-tube placed in a water bath. The pieces of metal are then shaken out into the water in the calorimeter, which is then vigorously stirred so as to bring about a



Fig. 13.—
Method of Mixture

rapid equalization of temperature. The temperature of the water in the calorimeter rises.

Let t_1 be the initial temperature of the water, t_2 that of the heated body, and t_3 that of the mixture. Further let the mass of the water be m_1 gm. and the mass of the body m_2 gm. We will calculate the quantity of heat that would be necessary to raise the temperature of each of the bodies concerned from 0° C. to that observed. We will call this their **heat content**.

The initial heat content of the water in the calorimeter was $m_1 t_1$ cal.; that of the heated body of specific heat c was $m_2 c t_2$ cal. Thus the total heat content before mixing was $(m_1 t_1 + m_2 c t_2)$ cal. Afterwards it is $(m_1 t_3 + m_2 c t_3)$ cal.

Assuming that there was no loss of heat during mixing, the total heat content before and after mixing must be the same. Hence we get the equation

$$m_1 t_1 + m_2 c t_2 = m_1 t_3 + m_2 c t_3,$$

whence

$$c = \frac{m_1 (t_3 - t_1)}{m_2 (t_2 - t_3)}.$$

In the above experiment the calorimeter itself was also heated up, as well as the thermometer and stirrer. In order to take this into account we calculate the water equivalent r of these three bodies from their known masses and specific heats. This must be added to the mass m_1 of the water in the calorimeter, so that the formula for c becomes

$$c = \frac{(m_1 + r) (t_3 - t_1)}{m_2 (t_2 - t_3)}.$$

If the calorimeter is made of very thin metal and if the masses of the thermometer and stirrer are also small, their water equivalent may be neglected for rough measurements.

A very accurate apparatus, which, however, is only suitable for a limited range of temperature, is the ice calorimeter (p. 69).

II. Specific Heats of Liquids.—These are determined just as in the case of a solid by heating up a known quantity of liquid and mixing it with water (or some other liquid of known specific heat) in a calorimeter: or a known quantity of the liquid to be investigated may be placed in the calorimeter and a hot body of known temperature and specific heat brought into it. In each case the final temperature of the mixture after equalization is observed. The total heat contents before and after mixing are then calculated and from them the unknown specific heat of the liquid. Another good method of determining the specific heat of a liquid is to add a calculated quantity of heat by means of an electric current passing through a wire dipping in it. (For the method of Callendar and Barnes, see Appendix.)

III. Specific Heat of Gases.—Since the density of a gas is relatively small, it is not possible to determine the specific heat by heating a certain volume and measuring the quantity of heat given up when it is mixed with water in a calorimeter. Hence a large amount of gas, previously raised to a high temperature, is led through a spiral tube (fig. 14) situated in a calorimeter *K* filled with water. The temperature of the entering gas is measured at *A*, that of the out-flowing gas at *B*. The gas cools down in passing through the tube and thus warms up the water in the calorimeter. The specific heat of the gas can then be calculated from the observed rise in temperature of the water and the mass and fall in temperature of the gas.

In this experiment care must be taken that the gas flows out at *B* at as nearly as possible the same pressure as it enters at *A*. For this reason the bore of the spiral tube must be chosen as wide as possible. If the pressure of the gas falls during its flow through the calorimeter, we obtain a lower value for the specific heat than at constant pressure. The specific heat of a gas is therefore not completely defined unless the words "*at constant pressure*" are added. The specific heat of air at constant pressure is $c_p = 0.2375$. For other gases see Table III (p. 290).

The gas cools down in passing through the calorimeter. Since its pressure remains constant it therefore flows out with a smaller volume than it had upon entry. The experiment can also be imagined to be carried out in such a way that the pressure of the gas diminishes during its passage through the spiral to such an extent that it leaves *B* with exactly the same volume as it had when it entered *A*. The value obtained in this case is the specific heat of the gas *at constant volume*, c_v . The practical performance of this experiment is attended

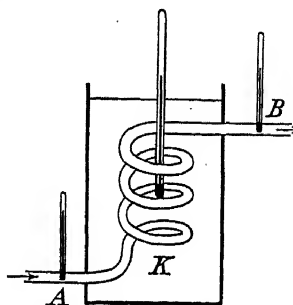


Fig. 14.—Determination of the Specific Heat of a Gas at Constant Pressure.

by great difficulties, and hence c_v is determined indirectly in a manner to be described later. The specific heat of air at constant volume is $c_v = 0.1690$. (Fuller details are given in the Appendix.)

It is found that the quotient $\gamma = c_p/c_v$ has almost the same value for all *diatomic* gases such as oxygen, nitrogen, and hydrogen, namely

$$\gamma = 1.4.$$

For *monatomic* gases (as for example helium, argon, and the other noble gases, also mercury vapour and zinc vapour) we obtain the value $\gamma = 1.67$. For *triatomic* gases, e.g. carbon dioxide and water vapour, $\gamma = 1.3$. As will be explained fully in § 1, p. 41, the still lower values given in Table III for alcohol and ether are due to the relatively complicated structure of the molecules of these gases.

2. Results of the Measurements of Specific Heats.—The specific heats of almost all substances are smaller than 1, i.e. smaller than that of water. Amongst solids an exception is lithium, which at 100° C. has a specific heat of 1.04. Ammonia liquefied under pressure also has a specific heat somewhat greater than unity. Amongst gases hydrogen with $c_p = 3.4$ and helium with $c_p = 1.25$ are worthy of mention.

The high specific heat of water explains the enormous influence of warm or cold ocean currents upon the climate of a land and also the difference between oceanic and continental climate. It finds practical use in hot-water heating. Table I gives the specific heats of a number of substances. Since the values vary with temperature it is necessary to state that those given only hold over a range from about 0° C. to 100° C.

The Dulong-Petit Rule.—In general the greater the specific gravity of a metal, the smaller its specific heat. The simple relationship between the specific heat and the *atomic weight* of solid elements was first discovered in 1819 by DULONG and PETIT* and is therefore known as the Dulong-Petit rule.

The product of the specific heat of a substance and its atomic weight is called the **atomic heat** of the substance.

The value of the atomic heat is approximately the same, namely 6.0, for all elements in the solid state.

In the case of chemical compounds the following rule (KOPP and NEUMANN) is of fairly wide validity.

The molecular heat of a compound (i.e. the product of its specific heat and molecular weight) is equal to the sum of the atomic heats of its constituent elements.

Under ordinary conditions of experiment the DULONG-PETIT rule is not a law

* P. L. DULONG (1785–1838), mostly occupied with chemical work, was severely injured in discovering nitrogen trichloride (NCl_3); later Director of the Polytechnic School at Paris. ALEXIS THÉRÈSE PETIT (1791–1820), Professor of Physics at the same

of nature; otherwise the deviations from it would not be so considerable. In spite of this the approximate equality of the atomic heats of the elements in solid form is very striking. According to the atomic theory weights of different elements in the ratio of their atomic weights contain equal numbers of atoms. Hence the above rule leads to the conclusion that equal numbers of atoms in any solid element require equal quantities of heat to raise their temperature by 1°C . (cf. p. 44).

Another striking thing is the *identity of the molecular heats* (at constant volume) of the different simple gases, both with one another and also approximately with the atomic heat of solid elements. Thus, for example, oxygen has the molecular weight 32, the specific heat at constant volume 0.154 and hence the molecular heat 4.928. The corresponding figures for hydrogen are M. Wt. = 2, $c_v = 2.414$, molecular heat = 4.828; and for nitrogen M. Wt. = 28, $c_v = 0.1729$, molecular heat = 4.841.

The respective atomic heats (at constant volume) of these diatomic gases (namely 2.46, 2.41, 2.42) are therefore approximately equal to one-half of the atomic heat of solid elements. Now the atomic heat of the monatomic gas argon has been found to be 2.9984, that of the monatomic gas helium 2.949, and of monatomic mercury vapour 2.99, i.e. approximately the same value in each case. Thus a kind of Dulong-Petit law appears to hold also for gases, being most accurately obeyed by monatomic gases.

The atomic heats of gaseous elements have approximately the same value, namely 3, i.e. one-half of that for elements in the solid state.

The atomic heats of the above-mentioned diatomic gases are smaller than those of the monatomic gaseous elements by about one-sixth of their value. The explanation of these relationships will be given on p. 44 *et seq.*

3. Dependence of Specific Heat upon Temperature.—The explanation of the deviations from strict obedience to the Dulong-Petit rule lies in the fact that the specific heats of substances are not true constants but vary with the temperature. At very low temperatures there is a decrease in the specific heats of all substances; at the absolute temperature the value zero would probably be reached (see further figs. 3 and 4, pp. 45 and 46). The rate of this decrease is different for different substances. Thus whereas in the case of metals there is a fairly steep fall of specific heat at very low temperatures, the values for carbon and also for silicon and boron decrease gradually and continuously with decreasing temperature at room temperature. Conversely the specific heats of many bodies increase when the temperature is raised above the normal; this is particularly marked in the case of carbon. Whereas the atomic heat of diamond at room temperature has the smallest known value of 1.35, at 1000°C . it has risen to about 6, the value for most other solid elements. From this it follows that the Dulong-Petit rule is a limiting law: the higher the temperature and the more nearly the specific heat of the substance has attained its maximum limiting value, the more closely the rule is obeyed.

8. Heat and Work. The Mechanical Equivalent of Heat

1. Transformation of Work into Heat.—It is a matter of everyday

experience that a body becomes warm when its motion is resisted and its kinetic energy consequently reduced.

In sawing a board—especially when the saw is blunt and binds, i.e. when a great deal of work must be expended in moving it—the blade of the saw becomes so hot that it cannot be touched without burning the fingers. In filing a piece of steel both the steel and the file become very hot, particularly when the former is placed upon wood, which has only a small power of conducting away the heat developed. There is also a marked rise in temperature during the hammering of lead, since the hammer does not bounce back from the blow; but the effect is much less marked when a piece of (cold) steel or iron is hammered, in which case the hammer springs up again to a considerable height after the impact, and has its kinetic energy only partially destroyed. The metal shavings from large metal-planing machines are so hot that there is a hissing sound when they fall into water. Lighter metals (especially magnesium alloys) may catch fire spontaneously when being turned in a lathe. If a piece of ordinary wood be rotated rapidly in a lathe and touched with a small piece of hard wood it will become so hot at the point of contact that it will be charred. Lead shot become warm when vigorously shaken up in a cardboard box; the same is true of mercury shaken in a vessel.

The most ancient method of producing fire, which is still in use amongst savages, consists of rapidly spinning a stick of hard wood in contact with a piece of softer wood. During this process the shreds of wood scraped off are first charred and finally burst into flame. The sparks produced by the impact of flint and steel also owe their origin to the heat of friction, the detached fragments of steel being raised to combustion temperature. The same process is also used in modern automatic lighters, which are provided with a piece of “cerein”, the splinters of which, when scraped off, are heated up to combustion and then ignite the petrol vapour above the saturated wick.

The production of frictional heat is often demonstrated by means of the following lecture experiment. A thin-walled brass tube closed at one end is placed upon a whirling machine, filled with ether and closed with a tightly fitting stopper. It is set into rotation and its motion suddenly braked by means of two pieces of cork pressed tightly against it with a clamp. The tube becomes hot, the ether evaporates, and the vapour blows the stopper out with a loud explosion.

2. **Historical.**—Although the fact that friction between bodies produces heat was known in earliest times, there was no clear conception of the nature of heat until comparatively recently.

The view that heat is a form of motion was expressed by individual thinkers at an early date (F. BACON) and also later by BOYLE, HUYGENS, NEWTON, DANIEL BERNOULLI, EULER, LAVOISIER, and LAPLACE. But the predominant opinion up to the first forty years of the nineteenth century was that heat was a substance (known as *caloric*).

Thus, for example, BLACK explained the difference of the specific heats of different substances by saying that the same quantity of caloric had a greater power of heating mercury than of heating an equal mass of water. It was only possible to account for the production of frictional heat by assuming that the specific heat of the particles detached during sawing, planing, and filing was smaller than that of the substance in bulk.

BENJAMIN THOMPSON (COUNT RUMFORD) * observed (1798) during his term

* BENJAMIN THOMPSON, born in North America in 1753, died at Paris in 1814, fought in the War of American Independence on the English side. In 1780 he was appointed English Secretary for State, and from 1782 was at the head of a squadron. After peace was made he entered the service of the Prince of Bavaria, in which he

of office in the arsenal at Munich that a considerable amount of heat was developed in the boring of cannon barrels. By placing the metal and the blunt borer in water he was able to bring this to the boil in $2\frac{1}{2}$ hr. From the quantity of water and the initial temperature he calculated that 26.6 lb. (= 12.07 kg.) of water could have been heated in this time from freezing-point to boiling-point. The energy required to drive the borer was furnished by two horses. Rumford maintained that it could have been furnished by one horse. In this case a certain amount of fodder would have had to be given to the horse to revive its capacity for work. Rumford deduced that it would be possible to produce the same quantity of heat by using this amount of fodder directly as fuel. He pointed out further that the frictional heat produced was inexhaustible, i.e. that he could produce as large a quantity as desired from the same piece of metal by letting the horse work a sufficiently long time. This was incompatible, however, with the hypothesis that heat is in the nature of a *substance*. Thus Rumford finally came to the conclusion that the only explanation of the production of heat through motion was to be found in the hypothesis that *heat is itself a form of motion*. He discarded the previously accepted theory that the fragments detached in sawing, boring, and powdering have a smaller specific heat than the body from which they are formed; for, as he proved, the borings actually possess the same specific heat as the bulk metal. Moreover he obtained the same quantity of heat when he used a *blunt* borer which produced no borings at all.

One year later (1799) SIR HUMPHRY DAVY* proved that the explanation of frictional heat as due to a diminution of specific heat was untenable by rubbing together two pieces of ice at -2° C. in an air-free space protected against radiant heat. This caused the ice to melt, although the specific heat of water is greater than that of ice.

In spite of these fundamental experiments, which were incompatible with the hypothesis of a heat substance, the old view was not given up. Even SADI CARNOT † whose work has become of great importance for the development of the science of heat (p. 111, *et seq.*), based his arguments and calculations upon the assumption that *heat cannot be destroyed or created*. From the sketches he left behind, however, it is clear that he gave up this assumption shortly before his death. But these notes, which were not published till 1878, had no influence upon the development of the subject. CLAPYRON (p. 16), who did valuable work in developing CARNOT's ideas (especially by his graphical representation of CARNOT's cycle, 1834) maintained the constancy of the quantity of heat in all thermal processes. On the contrary SÉGUIN declared himself in 1839 definitely in favour of the theory that there must be an "*identité de nature*" between heat and motion, and that the two must be different forms of effect arising from the same cause.

distinguished himself in many ways (introduction of potatoes and laying out of the English Garden in Munich, &c.), becoming lieutenant-general and receiving the title of COUNT RUMFORD. Then in 1799 he became one of the founders of the Royal Institution in London. He went to Paris in 1803.

* SIR HUMPHRY DAVY, born in 1778 at Penzance, was first a surgeon's apprentice in 1795 and then a chemist at Bristol in 1798. In 1801 he became Professor of Chemistry at the Royal Institution in London. He was President of the Royal Society from 1820 to 1827. His chief work was of a chemical nature. He discovered potassium and sodium, which he prepared with the electric current by electrolysis. His name is also connected with the miner's safety lamp. His experiment described above was of importance for the development of thermodynamics. He died in 1829 while on a visit to Geneva.

† SADI CARNOT, born in 1796 in Paris, entered the French engineer corps in 1814 and was appointed captain in 1826. He left the army in 1828 and died of cholera in Paris in 1832. His treatise *Réflexions sur la puissance motrice du feu . . .*, in which he published the cyclical process named after him, appeared in 1824.

Hence although the essential identity of heat and motion had been suspected by different thinkers at a much earlier date, it is undoubtedly the Heilbron doctor ROBERT MAYER's* distinction (1842) to be the first to deduce with complete clearness that a definite *numerical relationship* must exist between heat and work, and to calculate its value.

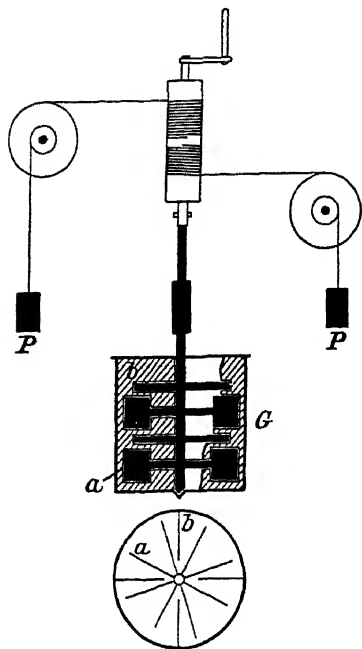


Fig. 15.—Diagram representing Joule's Apparatus for determining the Mechanical Equivalent of Heat.

Without being acquainted with Mayer's conclusions JOULE† determined this relationship experimentally by various methods and using different substances. In one of his pieces of apparatus a certain measurable amount of work was expended in moving a paddle-wheel in a cylindrical vessel containing water or mercury. This arrangement is represented diagrammatically in fig. 15. The two weights PP are raised through a certain height h by means of the crank-handle in the middle, the coupling between the axle and the paddle-wheel being disengaged. The paddle-wheel, which is capable of rotation in a cylindrical vessel G serving as calorimeter, is then coupled with the axis. When now the weights fall through the same distance h , their motion is braked by the paddle-wheel and the temperature of the calorimeter and its contents is raised. If W is the total

water equivalent and t° C. the rise in temperature, the quantity of heat obtained from the mechanical work Ph expended is $Q = Wt$.

JOULE also determined the heat produced by rubbing two metal plates together in a calorimeter.

* JULIUS ROBERT MAYER, born in 1814, was the son of an apothecary in Heilbron, studied medicine at Tübingen from 1831 to 1837. On a voyage to Java as ship's doctor he made the observation in 1840 that the venous blood is not so dark in colour in the tropics as in colder regions. In seeking for an explanation of this he became involved in considerations, partly of a philosophical and partly of a physical nature, concerning the relation between heat and work. Since he lacked a thorough physical and mathematical education, it is not surprising that POGGENDORF, the editor of the *Annalen der Physik*, refused to accept MAYER's first treatise. The true essence of his theories was not sufficiently easily discernible in face of the established concepts and doctrines of physics. Even a later and considerably clearer treatise, which appeared in 1842 in LIEBIG's periodical the *Annalen der Chemie und Pharmazie*, under the title "Bemerkungen über die Kräfte der unbelebten Natur" (Remarks upon the forces of inanimate nature), attracted but little attention. In his short treatise MAYER starts out from the fundamental principle "*causa aequat effectum*", which he interprets in the sense: "the cause is equal to the effect". Thus if heat is caused by motion, heat must be motion. The great value of MAYER's work does not lie in this assertion, which had indeed been made by others—especially COUNT RUMFORD—before him, but in his numerical calculation of the relation between work and heat. The values of the specific heats of gases used by MAYER as the basis of his calculation differ not inconsiderably from the values accepted to-day, and hence there is also a difference between the results of MAYER's and more modern calculations. He himself

JOULE's experiments led HELMHOLTZ † to write his classical treatise *Über die Erhaltung der Kraft*, in which he extended the principle of the conservation of energy to all types of phenomena.

3. Mechanical Equivalent of Heat.—The numerical factor by which a given quantity of heat is reduced to an equivalent quantity of work is called the *mechanical equivalent of heat*. The far-reaching importance of this constant is due to the fact that it expresses a connexion between two completely different groups of phenomena.

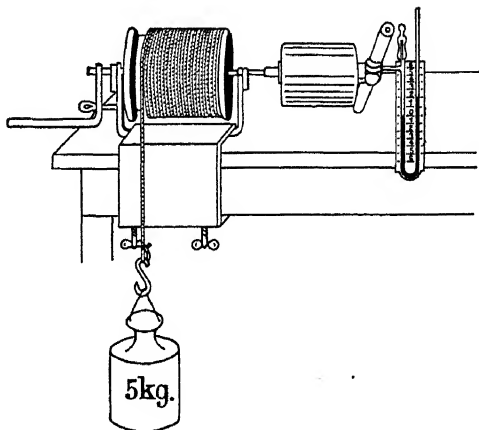


Fig. 16.—Grimsehl's Apparatus for determining the Mechanical Equivalent of Heat

Fig. 16 shows an apparatus (after GRIMSEHL) by means of which it is possible to demonstrate as a lecture experiment the production of frictional heat and the quantity of work expended. The falling weight sets in rotation an axle, on the prolongation of which is a cylinder of wood with a conical hole bored in it. A hollow copper cone is pressed into this hole and held at rest

did not carry out any practical experiments. In 1841 he returned to his native town as doctor. Although not a physicist and little recognized at first among physicists, he dedicated his time and work chiefly to the foundation and extension of the principle of the equivalence of work and heat in the organic and inorganic world. He died in 1878 at Heilbronn, misunderstood and embittered to the end.

† JAMES PRESCOTT JOULE, born 1818 at Salford, Manchester, died 1889 at Sale, was the owner of a brewery in his native town. He soon began to occupy his time with experimental investigations of electromagnetic phenomena and of the heat developed by an electric current in a conductor. These then led him (from 1843 onwards) to undertake experimental researches upon the relation between heat and work. He finally carried out important investigations on the thermal phenomena accompanying change of volume in gases (p. 106).

‡ HERMANN VON HELMHOLTZ, born 1821 at Potsdam, studied medicine in Berlin from 1838 to 1842. He then became assistant physician at the Berlin *Charité*, and in 1848 anatomy teacher at the *Kunstakademie* in Berlin. In 1849 he became Professor of Physiology at Königsberg, later took up positions at Bonn (1855) and Heidelberg (1858), and finally as Professor of Physics at Berlin (1871). In 1888 he was appointed President of the newly founded *Physikalisch-Technische Reichsanstalt* at Charlottenburg, an office which he held until his death in 1894. His scientific experiments were chiefly concerned with problems of physiology and physics. In the former subject he became famous on account of his invention of the ophthalmoscope, as well as for his fundamental works *Handbuch der Physiologischen Optik* and *Lehre von der Tonempfindungen*. In the realm of physics his above-mentioned treatise *Über die Erhaltung der Kraft* was of a pioneer character. In it HELMHOLTZ made no mention of the meritorious work of ROBERT MAYER. The treatise contains a critical survey of the then known experiments and a résumé of the results on the basis of the general principle of the conservation of energy. He also published a large number of scientific works, of an equally fundamental character, upon electrodynamics, thermodynamics, optics, and hydrodynamics.

by means of a cross handle while the wooden cylinder rotates. The copper is heated on account of friction with the wood, and the air inside it expands and moves the liquid in an open manometer connected as in the figure. The water equivalent of the cone and also the change of temperature corresponding to one scale division of the manometer being known from previous experiment, it is possible to calculate the quantity of heat produced and hence to determine its relationship to the work performed by the falling weight.

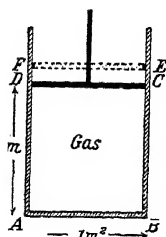


Fig. 17.—Ideal Experiment of R. Mayer

In 1842 ROBERT MAYER calculated the numerical relationship between work and heat in a purely theoretical manner from the difference of the specific heats of gases at constant pressure and constant volume (p. 23). For this purpose he considered the following ideal experiment.

Let ABCD (fig. 17) represent the vertical section through a prism-shaped box, the area of whose base is 1 m^2 . The box is closed by an air-tight frictionless and weightless piston CD at a distance of 1 m . from the base. The space enclosed is filled with air at 0° C . and 760 mm . pressure. Now imagine the air to be heated by 1° C ., the piston being held at rest so that the volume remains constant (case 1). Alternatively (case 2), imagine the rise of temperature to occur with the piston movable, so that the pressure of the air remains constant and the piston is raised to the position EF.

The original volume of the air considered is 1 m^3 . Now 1 cm^3 of air has the mass 0.001293 gm . at 0° C . and normal pressure, and hence the mass of the air enclosed in the box is $m = 1.293 \text{ kg}$. The specific heat of air (p. 23) at constant volume is $c_v = 0.169$, at constant pressure $c_p = 0.2375$. Hence the quantities of heat required to produce the change of temperature in the two cases are respectively mc_v and mc_p . The second quantity is greater than the first by $m(c_p - c_v) = 1.293(0.2375 - 0.169) = 1.293 \cdot 0.0685 = 0.0886 \text{ Cal}$.

Now in the second case the piston is raised through the height between CD and EF. The atmospheric pressure upon the piston is thereby overcome through this distance, i.e. work is performed. Since the atmospheric pressure is $1.033 \text{ kg. wt. per cm}^2$ (Vol. I), the total thrust upon the piston is $P = 10,330 \text{ kg. wt.}$ The height through which this is raised is equal to that by which the air column 1 m . in length expands according to Gay-Lussac's law when heated through 1° C . The coefficient of expansion of gases is 0.00367 and hence $h = 0.00367 \text{ m}$. The work done is therefore

$$Ph = 10,330 \cdot 0.00367 = 37.91 \text{ m. kg. wt.}$$

This must be equivalent to the excess of heat in the second case, namely 0.0886 Cal . Therefore 1 Cal. is equivalent to $37.91/0.0886 = 427.9 \text{ m. kg. wt.}$ As was known to R. Mayer, the assumption of

this method of calculation* is that a simple volume increase of a gas against zero pressure requires no heat (§ 6, p. 105).†

In 1858 HIRN ‡ determined the mechanical equivalent of heat by means of collision experiments with the apparatus represented diagrammatically in fig. 18.

He suspended a large block of stone *S* of 941 kg. wt. from a fixed frame by means of four strong ropes, so that it could execute pendulum swings in a direction parallel to itself. Immediately in front of it was an iron cylinder *H* of 350 kg. wt. suspended in the same way. This served as hammer and the stone block as a kind of anvil. The face of the block turned towards the iron cylinder was protected with an iron plate *E*, and just in front of it was suspended a lead cylinder *B* of 3 kg. wt. When the hammer was

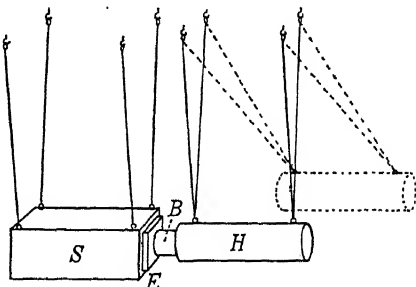


Fig. 18.—Hirn's Collision Experiment

raised out of its equilibrium position into that shown dotted in the figure, it possessed an amount of potential energy which could be calculated from its weight and the height through which it had been lifted. It was then let go and struck the lead cylinder. The stone block and the hammer moved together a small distance farther, rising slightly at the same time. The energy calculated from this small vertical rise and total weight was smaller than the original energy of the hammer. The difference had been transformed into heat, which had raised the temperature of the lead. The quantity of heat produced could be measured by allowing the lead to fall into a calorimeter. In this way HIRN found the value 452.2 m. kg. wt. per calorie for the mechanical equivalent of heat.

A very easily understood and instructive method of determining the mechanical equivalent of heat is that making use of WHITTING'S tube. This is a cardboard tube about 1 m. long and 6 cm. in diameter. The ends are closed with corks after 1 kg. of lead shot has been poured in. When the tube is turned say

* [Most English writers regard this assumption as a very serious flaw in Mayer's argument. Thus P. G. Tait (*Sketch of Thermodynamics*, 1877) remarks: "All three [Mohr, Séguin, Mayer] entirely ignore Carnot's fundamental principle, viz., that no deduction whatever can be made as to the relation between heat and mechanical effect, when the body operating or operated upon is in different states at the beginning and end of the experiment." "Mayer . . . enunciated and applied a false principle, and got (from the experiments of others on the specific heats of air) a widely erroneous result, which was improved, not by its author but by Joule, two or three years afterwards; who, after finding the true result by a legitimate process proved by experiments on air that Mayer ought to have got a good approximation."

Again, J. K. Roberts (*Heat and Thermodynamics*, 1928) says: "The calculation was of no actual value, until Joule showed later that the internal energy of a gas was to a close approximation independent of its volume."]

† One year later L. A. COLDING (1818–89) of Copenhagen made communications to the Copenhagen Scientific Society upon the connexion between heat and work. These were based originally upon considerations of a speculative nature. He followed them up later with experiments and determined the mechanical equivalent of heat by a frictional method, obtaining the value 350 m. kg. wt. per Cal.

‡ GUSTAV ADOLF HIRN, born 1815 at Logelbach near Kolmar, was a physicist and engineer at Kolmar, began his investigations of the mechanical equivalent of heat in 1843 and continued them in the meteorological observatory founded by him near Kolmar in 1880. He died at Kolmar in 1890.

100 times through 180° so that each time it finishes up vertical and the shot falls the whole distance from one end to the other, the temperature of the shot is raised by about 6°C . From the mean total distance of fall, the weight, the specific heat, and the rise in temperature of the shot it is possible to calculate the mechanical equivalent of heat.

Experiments carried out with extreme care (see Appendix) have finally led to the following values for the *mechanical equivalent of heat*:

1. *The quantity of work equivalent to the 15°C .-gramme-calorie (cal.) is*

$$4.185 \cdot 10^7 \text{ ergs} = 0.4268 \text{ m. kg. wt.},$$

the value of g being measured at 45° latitude and at sea-level, viz. $g = 980.6$.

2. *The quantity of work equivalent to the mean (0°C .– 100°C .) calorie is the same as in the case of the 15°C .-calorie.*

3. *The heat equivalent of the joule is equal to 0.23895 15°C .-calorie.*

In future we will designate the work equivalent of the 15°C .-calorie in absolute units by J and the heat equivalent relative to the same units by K . Then

$$J = 4.185 \cdot 10^7 \text{ ergs per } 15^\circ \text{C-cal.} = 4.185 \text{ joules per } 15^\circ \text{C-cal.}$$

$$K = 1/J = 0.23895 \cdot 10^{-7} \text{ } 15^\circ \text{C-cal. per erg} \\ = 0.23895 \text{ } 15^\circ \text{C-cal. per joule.}$$

If we wish to transform a given amount of mechanical work W into the equivalent quantity of heat Q , we must multiply W by K . The result is then obtained in cal. Conversely if we wish to transform a given quantity of heat Q into mechanical work, we must multiply Q by J . Thus we have

$$Q = KW, \quad W = JQ.$$

9. The First Law of Thermodynamics (Principle of Energy)

The law that *heat and work are equivalent* is known as the **first law of the theory of heat** or the **first law of thermodynamics**. It is an extension of the law of conservation of mechanical energy enunciated in Vol. I; for it states that when, for example, a certain amount of kinetic energy disappears with production of heat, then an equivalent quantity of heat is produced in its place. The newly appearing energy is equal in quantity to the energy which has disappeared. The same equivalence also holds for the reverse transformation. *The total energy is therefore constant.*

Hence, as was first perceived by J. R. MAYER, the generalized statement of the law of the conservation of energy runs as follows:

If a certain quantity of energy of any kind disappears in a process, then an equal quantity of energy of some other kind appears.

It is therefore impossible to conceive a process capable of producing energy, e.g. mechanical work, continuously out of nothing. The proof of this is furnished by the universal failure of all attempts to construct a perpetual motion machine,* i.e. a machine capable of producing a greater amount of work than the energy expended in driving it. Hence the energy principle can also be stated as follows:

It is impossible to construct a perpetual motion machine.

We will also express the first law of thermodynamics in a mathematical form.

When a certain quantity of heat energy dQ is communicated to a body, it may be transformed into a number of other energy forms. We will restrict our consideration for the present to mechanical and thermal changes. These consist of: (1) change of volume; (2) change of temperature; (3) change of molecular condition, e.g. of state of aggregation.

As a rule the volume of a body is increased by heating. We can consider the volume increase dV as an outward displacement of each element $d\Omega$ of surface area through the small distance ds . If the surface is subject to a normal pressure p (e.g. that of the atmosphere), the thrust on each element of surface area is $p d\Omega$ and the corresponding mechanical work done during the expansion is

$$dW = p d\Omega ds.$$

The whole body therefore performs the *external work*

$$dW = \int p d\Omega ds = p \int d\Omega ds$$

against the pressure. Now $\int d\Omega ds$ is equal to the change in volume dV . Hence the external work is

$$dW = p dV.$$

Since this work is a part of the effect of the heat energy dQ , we will express it in thermal units, thus obtaining

$$K dW = K p dV.$$

As will be explained in the next paragraph, the temperature of a body must be considered as due to the motions of its molecules. We know further that forces act between the molecules, determining their mutual distances and equilibria. In virtue of their motions the molecules possess *kinetic energy*, and because of the molecular forces they must also possess a certain *potential energy* corresponding to the state of the body. The sum of these energies is given the name *internal energy* or *energy content* of the body. If the temperature and the molecular condition are altered by addition of heat, the internal

* Cf. footnote, Vol. I, p. 354.

energy of the body is changed. We will call this change the *internal work* performed by the heat and designate it by dU in mechanical measure and by $K dU$ in thermal measure. This internal work is the second part of dQ .

Neglecting for the present all other changes which can be caused by the addition of heat (in particular electric or magnetic changes), we therefore have the equation

$$dQ = K(dU + p dV).$$

This equation is the mathematical expression of the first law of thermodynamics. It was first stated in this form by R. CLAUSIUS.*

Internal Energy of a Gas.—From the equation given above we will make a further deduction which will be useful later:

Let the temperature of a body be raised by the amount dT by the addition of a quantity dQ of heat. Then in order to raise the temperature 1° a quantity of heat dQ/dT will be required. This is the specific heat c of the body. Making use of the equation for the first law we obtain therefore

$$c = \frac{dQ}{dT} = K \left(\frac{dU}{dT} + p \frac{dV}{dT} \right).$$

In the case of a gas we have to distinguish between the specific heats at constant volume and constant pressure. In the former case we have $V = \text{const.}$ and therefore $dV/dT = 0$. Hence there is no external work done when a gas is heated at constant volume. Thus in this case

$$c_v = K \frac{dU}{dT}.$$

From this it follows that $dU = Jc_v dT$, or integrating between the limits T_0 and T

$$U = \int_{T_0}^T Jc_v dT = Jc_v (T - T_0).$$

If we make the further assumption that the internal energy of a gas vanishes at the absolute zero, we have

$$U = Jc_v T.$$

This equation can be expressed in words as follows:

The internal energy of a gas is proportional to its absolute temperature.

It was assumed above that the specific heat of the gas at constant volume does not vary with temperature; such a gas is an ideal gas in the sense of p. 15.

Since the last equation does not contain either p or V , it follows that:

The internal energy of a gas is independent of its pressure and volume.

If the volume and pressure of a gas alter at constant temperature, the internal energy remains unchanged.

For the experimental investigations on this subject, see § 6, p. 105.

* RUDOLF CLAUSIUS, born 1822 at Köslin, in 1855 became Professor of Physics at the Polytechnic College and the University of Zürich; in 1867 he went to Würzburg in the same capacity, in 1869 to Bonn, where he died in 1888.

CHAPTER II

Kinetic Theory of Heat

1. Gases

1. **Kinetic Theory of Gases.**—It has already been mentioned above that the heat energy of material bodies is to be regarded as energy of motion, i.e. in accordance with our knowledge of the structure of matter (Vol. I, p. 261), energy of motion of the molecules. Since every body at a temperature above the absolute zero possesses heat energy, we must consider the molecules in all the bodies which we can investigate as being in unceasing motion.

One of the most impressive experiments in this connexion is the following. A fine water suspension of any insoluble substance (e.g. a dye) is viewed under the microscope. The whole field of view is then seen to be filled with a teeming, irregular motion, although we are dealing with a "dead, inorganic" substance. (Brownian movement.) This is a direct observation of heat motion. The same can also be seen with the aid of a microscope in the case of smoke particles suspended in the air. A more detailed discussion of this phenomenon will be found in § 2, p. 54.

A number of other phenomena also lead to the conclusion that under ordinary conditions the molecules must be in rapid motion.

Thus if a gas jar containing the very dense brown gas bromine be closed with a cover slip and a well fitting jar full of air inverted over it, the bromine will spread up into the air when the slip is withdrawn, although its density is much greater than that of air. The process can be followed easily on account of the brown colour. There is no macroscopic motion (i.e. motion visible to the naked eye) or flow in the gas, as can be proved by inserting very light bodies which would be moved by the smallest current. From this we conclude that in spite of its apparent state of rest the gas possesses an irregular internal molecular motion, by virtue of which the molecules can advance considerable distances in a few seconds in spite of the zig-zag nature of their paths.

It will be particularly simple to follow the regularities of this motion in the case of gases, for here the forces of cohesion are scarcely noticeable (Vol. I). Our mental picture of a gas must be as follows.

An extremely large number of tiny particles, the molecules, to which we can ascribe elastic properties, move about with high velocities like a

confused swarm of minute billiard balls, frequently colliding with one another and rebounding vigorously. In general the forces of attraction are quite ineffective, because the lengths of time during which the molecules are sufficiently close together are far too short. This way of picturing a gas is called the *kinetic theory of gases*.

The science of heat as a form of motion was developed especially by CLAUSIUS from 1857 onwards.

He had recognized that the conditions of motion must be very simple in the case of gases, because here the molecules have the greatest freedom. Although KRÖNIG* had investigated gases a year earlier with regard to their molecular motion, it is the achievement of CLAUSIUS to have developed in detail the science of the motion of gaseous molecules as the explanation of heat energy.

According to the simplest assumption of the kinetic theory the individual molecules in a space filled with an ideal gas under no forces move in straight lines with complete freedom and without any interaction (except for completely elastic collisions) (§ 10 and § 11, p. 138 *et seq.*). The molecular velocities, which are very great, depend only upon the nature of the gas and upon its temperature. We may remark in advance that air molecules, for example, move with a mean velocity of about 500 m. per sec. (p. 47) at 0° C. In spite of this, the distances traversed by the individual molecules between chance encounters with other molecules are only small (on an average $1 \cdot 10^{-5}$ cm. (p. 50)). The reason for this is that there is such an extraordinarily large number of molecules present. At normal atmospheric pressure and 0° C. there are about $27 \cdot 10^{18}$ molecules (p. 53) in a cubic centimetre.

In order to give an idea of the magnitude of this number it may be stated that, continuing day and night at the rate of 100 per minute, the time required to count up to it would be more than 500,000 million years.

The diameter of each individual molecule is of the order of $5 \cdot 10^{-8}$ cm. (p. 53) and their mean distance apart is $3 \cdot 10^{-7}$ cm. Each molecule in 1 cm.³ of air makes about 5000 million collisions every second. The numbers given are averages deduced theoretically from experimental results.

The impacts of the gas molecules upon the walls of the containing vessel are the cause of its pressure. Thus the pressure of a gas is not to be regarded as a statical elastic pressure but as a dynamical effect due to a molecular bombardment, similar to the dynamical pressure exerted by a jet of water directed against a flat surface.

In the light of the kinetic theory we can explain why a gas always occupies the whole of the space at its disposal. For in the case of a gas enclosed in a cylindrical space by means of a movable piston the molecules collide at frequent

* A. K. KRÖNIG (1822-79), high school headmaster. The first to perform accurate calculations in this direction appears to have been J. J. WATERSTON, who sent in a paper on the subject to the Royal Society in 1845. The paper was, however, refused. He thus had the same experience as J. R. MAYER shortly before in Germany.

intervals and bounce off each other like completely elastic spheres; they also strike against the cylinder walls and the piston and rebound from them. Now imagine the piston, which so far has been held at about the middle of the cylinder, to be withdrawn suddenly. Instead of rebounding from it as before, the rapidly moving molecules will now be able to penetrate freely into the new part of the cylinder before they are turned back.

2. Calculation of the Pressure of a Gas by the Kinetic Theory.—

Let V be the volume of the vessel, n the number of molecules enclosed in it, m the mass of each molecule, c the mean velocity of the molecules,* p the pressure of the gas (per unit area, cm.²) and E the total kinetic energy of all the molecules enclosed in the vessel. Then at constant temperature the following equation holds:

$$p = \frac{nm c^2}{3V} = \frac{2E}{3V}.$$

We will prove this equation only for the special case of a hollow spherical vessel of radius R ; the proof can, however, be extended to vessels of any other shape. We will simplify the calculation by assuming that the molecules do not collide. This is permissible and introduces no error; for when two molecules, considered as similar and completely elastic, collide "head on", they simply exchange their velocities, i.e. the result is exactly the same as if they had passed freely through each other; when the collision is oblique, the directions of motion are also changed, but the total energy remains unaltered.

An elastic sphere of mass m , impinging normally with velocity c upon a fixed wall, is turned back without change of magnitude of its velocity; but its direction is reversed, i.e. c is changed into $-c$ and the momentum mc into $-mc$. Thus the change of momentum is $2mc$. We can imagine this change as due to a force of impulse $2mc$ exerted upon the sphere by the wall. According to the principle of the equality of action and reaction the wall must also be subjected to the impulse $2mc$ in the same time. If the direction of motion of the sphere before impact makes an angle ϕ with the normal to the wall, then only the component of the impulse perpendicular to the wall, namely $2mc \cos \phi$, is effective.

The gas molecules in the spherical vessel (fig. 1) behave like the elastic spheres just considered. Each molecule rebounds from its impact with the inner surface of the sphere at the same angle ϕ as its angle of incidence. It then strikes the wall again later at the same angle and so on. Thus between two successive impacts the molecule considered always traverses the same distance $s = 2R \cos \phi$. Since its velocity is c , it must strike the wall $c/(2R \cos \phi)$ times per second. Now each impact is associated with the impulse $2mc \cos \phi$, and hence the total impulse of all the impacts in a second is

$$2mc \cos \phi \frac{c}{2R \cos \phi} = \frac{mc^2}{R}.$$

But according to the fundamental meaning of impulse the total impulse per second is numerically equal to the mean force over the same period. From the disappearance of ϕ out of the equation it follows that the force exerted upon the wall by a molecule is independent of its direction of motion.

* For the time being we will consider all the molecules as having the same velocity c .

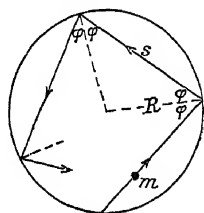


Fig. 1

Since there are n molecules present, the total force upon the whole inner surface of the vessel is nmc^2/R . The area of this surface being $4\pi R^2$, the pressure (per unit area) is

$$p = \frac{nmc^2}{4\pi R^3},$$

or since the volume of the sphere is $V = \frac{4}{3}\pi R^3$,

$$p = \frac{nmc^2}{3V}.$$

The kinetic energy of each molecule is $\frac{1}{2}mc^2$ and therefore the total kinetic energy of all the molecules is $E = \frac{1}{2}nmc^2$. Substituting this value we obtain the result to be proved, viz.

$$p = \frac{nmc^2}{3V} = \frac{2E}{3V}.$$

Writing this equation in the form $pV = \frac{2}{3}E$ and remembering that as long as the temperature does not change the total kinetic energy must remain constant on account of the assumed complete elasticity, we obtain Boyle's law:

$$pV = \text{const.}$$

3. Temperature.—The addition of heat to a gas at constant volume increases its internal energy. Now it follows from the first law (see p. 34) that the internal energy of a gas is directly proportional to its absolute temperature. But according to the fundamental hypothesis of the kinetic theory of heat this internal energy is nothing else than the kinetic energy of the gas molecules. Let T and U be the absolute temperature and internal energy of the gas respectively before the addition of heat, and T' and U' the respective values afterwards. Then we have (p. 34) $U : U' = T : T'$. On the other hand, however, $U = \frac{1}{2}nmc^2$, where n is the number of molecules in the space considered, m the mass of each and c the mean molecular velocity. In the same way $U' = \frac{1}{2}nmc'^2$. Hence $U : U' = \frac{1}{2}mc^2 : \frac{1}{2}mc'^2$, and in combination with the previous equation

$$T : T' = \frac{1}{2}mc^2 : \frac{1}{2}mc'^2.$$

This equation states that:

The absolute temperature of a gas is proportional to the kinetic energy and therefore to the mean square velocity of the molecules.

We may write this relationship in the form $LT = \frac{1}{2}mc^2 = E/n$, where L is a proportionality factor representing the mean kinetic energy of a gas molecule at the temperature $T = 1^\circ$ abs. The equation for p can then be transformed to

$$p = \frac{2LTn}{3V} \quad \text{or} \quad \frac{pV}{T} = \frac{2Ln}{3}.$$

The quantity on the right-hand side of the last equation is constant. Hence we may write

$$\frac{pV}{T} = R.$$

This is the Boyle-Gay-Lussac law and R is the gas constant referred to n molecules, i.e. $R = 2Ln/3$. As a mnemonic it may be remarked that the quantity $2L/3$ would be the gas constant for $n = 1$, i.e. referred to an amount of gas consisting of only *one* molecule. If by R we understand the gas constant for a gramme-molecule (one mol), n must be put equal to the number of molecules in a mol.

4. Temperature Equilibrium.—Experience teaches that when two quantities of the same gas at different temperatures are brought together, the temperatures equalize out and there results a mixture of uniform temperature throughout. When it is no longer possible to observe any temperature difference between any two space elements however small, we say that *thermodynamical* or *temperature equilibrium* has been reached. Before mixing, the molecules of the colder gas had a smaller mean velocity than those of the hotter gas (see above). At thermodynamical equilibrium the mean molecular velocities of the two quantities of gas must have become equalized owing to the numerous collisions. In the final state the velocities of all the molecules of the mixture lie around one mean value at any instant. In the same way the mean value of the velocities assumed by any selected molecule between successive collisions, i.e. the mean velocity of any molecule over a period of time, is equal to the mean velocity of all the molecules at any instant. The following consideration of a special case shows that such an equalization of velocity is a necessary result of the fundamental hypothesis of the theory. First consider all the molecules in a certain space to have zero velocity, i.e. to be at rest, relative to the boundary walls, and to be distributed completely at random. Imagine now a single new molecule to enter the space with high velocity. It will soon come into collision with one of the molecules at rest. If the collision is head on, then according to the laws of collision the moving molecule will come to rest, its motion being taken up completely by the molecule it strikes. On account of the finite size and random distribution of the molecules a far more probable case will be that in which the collision is oblique; the struck molecule will then move off with a fraction of the velocity of the striking molecule, which will be correspondingly slowed down and deflected. Both molecules will now soon collide with others at rest. A similar transference of velocity and energy will once more take place, until eventually all the molecules are involved. We see, therefore, that a final state will be reached in which all the molecules are in motion and continually sharing their energies. Since the total energy of the system remains constant and (in accordance with the assumed random distribution) no molecule is distinguished from the others, they must all eventually possess the same time average of kinetic energy. Thus the energy of the single moving molecule is distributed on the average uniformly amongst all the others; this is the characteristic of thermodynamical equilibrium.

5. Molecular Energy of Different Gases.—We have tacitly assumed above that the molecule entering the space was of the same kind and therefore of the same mass as those already present. How will the result be affected if the entering molecule is of another kind, and

possesses a different, say a much greater, mass? When the final state of thermodynamical equilibrium is reached, this one molecule will be distinguished from the others on account of its greater mass. It might therefore be thought that it would possess a greater or smaller mean energy than the others. It is difficult to reach a decision on this point by theoretical considerations, because the conditions are very complicated. We will therefore refer once more to experiment. Consider equal numbers of heavier and lighter gas molecules enclosed in a space at thermodynamical equilibrium. We can now imagine the two gases to be separated partially from one another without change of their molecular velocity. For this purpose use might be made, for instance, of the property that lighter gases diffuse more quickly than heavier ones through a porous wall. Thus if the space containing the gases were fitted with a porous wall, the lighter molecules would diffuse through into the adjoining space in greater numbers than the heavier ones. In this way the original space could be divided into two parts containing equal numbers of molecules, the one part containing an excess of the molecules with smaller mass, and the other an excess of those with greater mass. Experience teaches that the temperature must remain the same in both parts; for no case has ever yet been observed in which a difference of temperature appeared "of itself", i.e. without work being expended upon the system from outside (§ 9, p. 125). But the same equation of state with the same gas constant R holds (p. 16) for equal numbers n of molecules of all (ideal) gases. According to the last equation above (p. 38)

$$\frac{2Ln}{3} = R.$$

Hence L and consequently $LT = \frac{1}{2}mc^2$ have the same respective values for all gases.

At thermodynamical equilibrium the internal kinetic energy of an (ideal) gas is distributed on the average uniformly amongst all the molecules, no matter what their nature.

This law of the equality of the mean molecular energies of all gases at the same temperature is deduced here from AVOGADRO'S hypothesis (p. 16) in combination with the BOYLE-GAY-LUSSAC law. Conversely, AVOGADRO'S hypothesis follows strictly from the kinetic theory of gases, provided it can be proved that the mean molecular energy is independent of molecular mass at thermodynamical equilibrium. This proof was furnished in 1860 by CLERK MAXWELL with the help of fundamental calculations involving the theory of probability, and was completed in 1894 by LUDWIG BOLTZMANN.

6. Law of Equipartition of Energy at Thermodynamical Equilibrium.—This law has attained great importance in the theory of heat. It can be generalized at once as follows. Imagine the velocity

of a molecule to be resolved into three mutually perpendicular components c_x , c_y , and c_z . Then

$$LT = \frac{1}{2}mc^2 = \frac{1}{2}mc_x^2 + \frac{1}{2}mc_y^2 + \frac{1}{2}mc_z^2.$$

Since all the directions of motion of the gas molecules in the space considered are equivalent, the mean values of the squares of the component velocities must be equal, i.e.

$$\overline{c_x^2} = \overline{c_y^2} = \overline{c_z^2} = \frac{1}{3}c^2.$$

Thus we can imagine the mean kinetic energy of the molecules to be made up of three independent parts each associated with one of the co-ordinate directions and equal to $\frac{1}{6}mc^2$. We may express this by saying that the kinetic heat energy is equally distributed amongst the three co-ordinate directions.

If a molecule were not free to move in all directions, e.g. if it were constrained to move along a straight line, it would be restricted with regard to partition of its energy by collision. It would only be able to receive and impart blows in the direction in which it was free to move. The mean energy corresponding to this single direction is $\frac{1}{3}LT = \frac{1}{6}mc^2$. Hence by the law of equipartition the mean energy of the constrained molecule could only be $\frac{1}{3}LT$.

This kind of consideration is of great importance for the treatment of the kinetic heat energy of a solid. The molecule is then considered to oscillate about an equilibrium position. The freedom of motion of the molecules of a solid is thus limited in comparison with that of the molecules of a gas with which it is in thermodynamical equilibrium. The gas molecule has three space components of free mobility, whereas the molecule of the solid oscillating about a fixed equilibrium position has only one. We say that the gas molecule has three *degrees of freedom* and the linearly oscillating molecule of the solid has only one degree of freedom. The equipartition law then takes the following form.

At thermodynamical equilibrium the energy is distributed on the average uniformly amongst all the degrees of freedom of the molecule.

Now in the case of a molecule oscillating linearly about a mean position (a *linear oscillator*), as in every (harmonic) motion (e.g. that of a pendulum), the time mean of the kinetic energy is equal to the time mean of the potential energy. Thus the linear oscillator possesses the average amount $\frac{1}{2}LT$ of kinetic energy and the same average amount of potential energy. Its total energy is therefore $E = \frac{1}{2}LT = kT$. The constant k (BOLTZMANN'S constant) is the mean total energy of such a molecule at the temperature $+1^\circ$ abs. (For the numerical value see p. 60.) One share of energy is required, as it were, for the motion of the molecule and one for its displacement from the mean position.

If a gas molecule has a moment of inertia of considerable magnitude (see below), it may be set into rotation by collision. The molecule thus takes up rotational as well as translational energy as internal molecular energy. When

only one axis of rotation is possible, it follows from the MAXWELL-BOLTZMANN law of equipartition that the amount of energy corresponding to this one degree of freedom must also be $\frac{1}{2}LT$.

The law of the equipartition of energy has been stated by these investigators in a form covering all these cases, namely:

At thermodynamical equilibrium the thermal energy is distributed equally amongst all the independent parameters of state upon whose squares the energy depends.

By parameters of state (§ 11, p. 141) we have here to understand such quantities as velocity components, angular velocities, harmonic displacements, frequencies, &c., which determine the thermal state of the system considered. The law has proved to have wide validity not only in the theory of gases but also more especially in the theory of liquids and solids and even of heat radiation.

7. Most Appropriate Measure of Temperature.—According to the law of equipartition of heat energy it is possible to determine a certain numerical quantity for each parameter of state at thermodynamical equilibrium, namely the magnitude of the mean kinetic heat energy per degree of freedom, $\frac{1}{2}mc^2 = \frac{1}{2}LT$. This is therefore the most appropriate measure of temperature.

8. Molecular Heat.—In the case of an ideal gas whose molecules are assumed to be point masses and therefore to possess neither rotational nor internal vibrational energy (p. 142), the heat content Q is equal simply to the total kinetic energy of the translational motion of the molecules. Hence for n molecules we have

$$Q = E = \frac{1}{2}nmc^2 = LTn.$$

Since now $R = \frac{2}{3}Ln$ (see above), therefore $Q = \frac{3}{2}RT$, or for each degree of freedom $Q = \frac{1}{2}RT$. If c_v is the specific heat of the gas at constant volume and μ the molecular weight, then $\mu c_v = C_v$ is the heat capacity for a gramme-molecule, i.e. the molecular heat. The gas constant, R in mechanical measure or KR in thermal measure, is referred to one gramme-molecule, consequently

$$Q = T\mu c_v = \frac{3}{2}KRT \quad \text{and} \quad \mu c_v = C_v = \frac{3}{2}KR,$$

or for each degree of freedom

$$C_v' = \frac{1}{2}KR.$$

$$\text{Now } KR = 0.239 \cdot 10^{-7} \frac{\text{cal.}}{\text{erg}} \times 8.313 \cdot 10^7 \frac{\text{erg}}{\text{degree} \cdot \text{mol.}} \quad (\text{pp. 16 and 32}) \quad \text{and}$$

$$\text{hence} \quad \mu c_v = \frac{3}{2} \cdot 0.239 \cdot 8.313 = 2.98 \text{ cal.}$$

Thus the kinetic theory of gases requires the same molecular heat for all (ideal) gases (see also § 9, p. 34). It is worthy of note that the value derived from the theory has been almost exactly verified for monatomic gases, namely for argon (2.998), helium (2.949) and mercury vapour (2.99).

In the case of diatomic gases the molecular heat is considerably greater. From this it can be concluded that the molecules of these gases possess other energy parameters beside the velocity of translation; according to the law of equipartition these take up a part of the energy added. Thus, for example, the molecules may rotate or there may be vibrations of their constituent atoms. We will assume that there is merely a rotation of the molecule as a whole about an axis at right angles to the line joining the two atoms and passing through its middle point (see below). The molecule has two mutually perpendicular

principal axes of inertia of this kind. By the equipartition law the rotations about each of these independent axes of rotation must be associated with the mean energy $\frac{1}{2}mc^2$. The total rotational energy about the two axes is therefore $\frac{1}{2}mc^2$. Hence for n molecules the total energy (translational and rotational) is

$$\frac{1}{2}nmc^2 + \frac{1}{2}nmc^2 = E + \frac{2}{3}E = \frac{5}{3}E = \frac{5}{3}nLT.$$

Let this be the heat content of a gramme-molecule of mass μ . Then again

$$Q = \mu c_v T = \frac{5}{3}nLT = \frac{5}{3}KRT$$

and

$$\mu c_v = \frac{5}{3} \cdot 2.98 \text{ cal.} = 4.967 \text{ cal.}$$

This is the theoretical molecular heat for a diatomic gas. The actual values given on p. 25 for oxygen (4.928) and nitrogen (4.841) are not very different from the theoretical value. That for hydrogen (4.828) is somewhat lower (see below).

9. The Ratio of the Specific Heats $c_p/c_v = \gamma$.—When heat is added to a gas at constant pressure there is an increase of volume and hence a performance of external work. Thus the quantity of heat required to produce a rise of temperature $T_2 - T_1$ must be greater than at constant volume by an amount equivalent to the work performed. An increase of volume $V_2 - V_1$ at pressure p corresponds to the work $p(V_2 - V_1)$ or the equivalent quantity of heat $Kp(V_2 - V_1)$. If the specific heats at constant volume and constant pressure are respectively c_v and c_p , then for a gramme-molecule of mass μ the quantity of heat required to produce a rise of temperature $T_2 - T_1$ is

$$Q = \mu c_v(T_2 - T_1) + Kp(V_2 - V_1).$$

From the equation of state we have $p(V_2 - V_1) = R(T_2 - T_1)$ and hence

$$Q = \mu c_v(T_2 - T_1) + KR(T_2 - T_1).$$

But from above $KR = \frac{2}{3}\mu c_v$, therefore

$$Q = \mu c_v(T_2 - T_1) + \frac{2}{3}\mu c_v(T_2 - T_1) = \frac{5}{3}\mu c_v(T_2 - T_1).$$

For Q we can also write

$$Q = \mu c_p(T_2 - T_1).$$

It follows therefore that

$$\gamma = c_p/c_v = \frac{5}{3} = 1.667.$$

This requirement of the theory is fulfilled for *all* monatomic gases, argon, helium, mercury vapour, &c. (p. 24).

From this experimental verification of the value $\frac{5}{3}$ for γ we can deduce the fundamental equation of the kinetic theory of gases (p. 37). Thus if we substitute $\gamma = \frac{5}{3}$ in the equation $E = pV/(\gamma - 1)$ on p. 104 we obtain $E = \frac{3}{2}pV$. Here E has the same meaning as on p. 37, since according to the fundamental hypothesis of the kinetic theory the total energy content of a gas is equal to the kinetic energy of its molecules.

In the case of diatomic molecules the only modification is that now $KR = \frac{2}{5}\mu c_v$ (see previous subsection). It follows then that

$$Q = \mu c_p(T_2 - T_1) = \mu c_v(T_2 - T_1) + \frac{2}{5}\mu c_v(T_2 - T_1) = \frac{7}{5}\mu c_v(T_2 - T_1),$$

whence

$$\gamma = c_p/c_v = \frac{7}{5} = 1.40.$$

This equation is fairly well obeyed in the case of hydrogen, oxygen, and nitrogen (see Table III), for all of which $\gamma = 1.405$.

10. The Decrease of Specific Heat at Low Temperatures.—In the case of the atoms of a solid vibrating about fixed centres, the equipartition law states that the quantity of energy $\frac{1}{2}mc^2$ must be associated with each degree of freedom as mean kinetic energy and an equal quantity as mean potential energy (see above, p. 41). Hence, taking the number of degrees of freedom as 3, the atomic heats of a solid element must be twice as great as the molecular heat of an ideal monatomic gas, i.e. $2 \cdot 2.980 = 5.96$ cal. But this is the DULONG-PETIT rule. It is also possible to give a partial explanation of the deviations from it. One thing not accounted for by the treatment so far given, however, is the observed decrease of specific heat at very low temperatures. Since all bodies show this decrease, it must be due to some quite fundamental cause not embraced in the above theory. EINSTEIN was able to show that this behaviour could be accounted for on the basis of Planck's quantum theory (to be treated in detail in Vol. V), i.e. with the assumption that the molecules do not take up energy continuously when heated, but only in certain small units, the *energy quanta*. It is found that the size of these quanta (i.e. the amount by which the energy of a molecule can alter) depends upon the frequency ν of the molecule, the energy for each degree of freedom only altering by the amount $\epsilon = h\nu$ or an integral multiple of it. Here h is a universal constant (Planck's constant), the nature and significance of which will be discussed in Vol. V. We can obtain the approximate value of the frequency of the molecule from the following equation (LINDEMANN, 1910).

$$\nu = 2.8 \cdot 10^{12} \sqrt{\frac{T_f}{AV^{\frac{1}{3}}}},$$

in which T_f is the melting-point of the substance on the absolute scale, A its atomic weight and V the volume occupied by a gramme-atom. The line of thought leading to this relationship between melting-point and frequency is somewhat as follows. The more tightly an atom is held by those next to it, the less will it be displaced out of its mean position by temperature motion, i.e. the higher will be the melting-point of the substance. But the more tightly an atom is held by its neighbours, the greater is its frequency of elastic oscillation.

Accurate calculations show that it is necessary to assume a number of different frequencies ν in the same body.

The specific heat of a gas at constant volume was found above (p. 42) to be $C_v' = \frac{1}{2}R$ for each degree of freedom; but according to the theory of quantized distribution of energy the value for each degree of freedom in the case of a solid is

$$C_v'' = \frac{1}{2}R \left(\frac{h\nu}{kT} \right)^2 \frac{e^{\frac{h\nu}{kT}}}{\left(e^{\frac{h\nu}{kT}} - 1 \right)^2}.$$

* Considering only solids.

The symbols have the same meaning as above and k is the BOLTZMANN constant, $1.37 \cdot 10^{-16}$ (p. 41).

When ν/T is very small, i.e. when ν is very small (e.g. in the case of bodies of low melting-point) or when T is very large, the expression for C_v'' becomes identical with that for C_v' . On the other hand, when ν/T becomes large, C_v'' is smaller than C_v' ; in the limit when $\nu/T = \infty$, $C_v'' = 0$. Hence if ν remains constant and the number of degrees of freedom does not change, the specific heat must decrease with decreasing temperature.

The greater ν is, the smaller the contribution of each degree of freedom to the specific heat. Hence if, for example, the moment of inertia about one of the axes is very small, the corresponding period of oscillation (which is proportional to the square root of the moment of inertia) will also be small. The frequency ν will therefore be very large. At low temperatures ν/T will be large and hence the contribution of this degree of freedom to the specific heat will also be very small. It is therefore justifiable only to take into account moments of inertia of considerable magnitude and to neglect the others. As regards its mechanical properties, a diatomic molecule can be imagined to consist of two elastic spheres connected rigidly together at a distance which is large in comparison with their diameters (fig. 2, "dumb-bell" model). In this case both the mutually perpendicular axes a and b will correspond to degrees of freedom, but not the axis c . Hence such a model has $3 + 2 = 5$ degrees of freedom. Its molecular heat C_v must therefore be 4.967 cal. (see above). The moments of inertia about the axes a and b are in general not very large, particularly if the masses of the atoms are small, so that a decrease of the specific heat is to be expected at low temperatures. This is actually observed. Even at room temperature the value for hydrogen is considerably smaller than would correspond to the total number of its degrees of freedom. With decrease of temperature its specific heat becomes still smaller (EUCKEN, 1912). The following are the observed values:

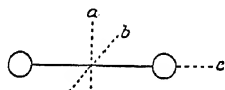


Fig. 2.—Dumb-bell Model of a Diatomic Molecule

$t =$	-76	-183	-233° C.
$T =$	197	90	40° abs.
$C_v =$	4.38	3.25	2.98.

Thus at -233° C. hydrogen has the specific heat of a monatomic gas, the rotational

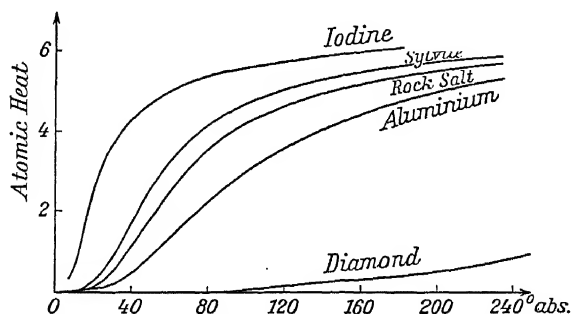


Fig. 3.—Dependence of Specific Heat of Solids upon the Temperature

degrees of freedom contributing scarcely anything to its value. These considerations only hold for degrees of freedom to which one can ascribe a frequency ν

(motions of oscillation or rotation). It is not possible to ascribe a frequency ν directly to the rectilinear translational motion of a gas molecule.

In the case of solids, where there is no translational motion of the molecules, the specific heat must decrease more and more with decrease of temperature. This is actually borne out by observation (fig. 3). This decrease will be most easily observable at comparatively high temperatures for substances for which ν is large, i.e. according to the formula on p. 44 for substances which have a high melting-point and a low atomic weight. The best examples are diamond, boron, and silicon. Even at room temperature diamond has a remarkably low atomic heat, namely 1.4 instead of 6 as demanded by the Dulong-Petit rule. At -183°C . the value is only 0.03 and at -230°C . practically zero. (NERNST-LINDEMANN.) In the case of boron and silicon the decrease also occurs at much higher temperatures than for the other elements. The frequency ν can be calculated from the formula on p. 44 or better from C_p'' ; it can also be obtained directly from optical measurements (residual rays, see Vol. V). The value obtained for diamond is $3.9 \cdot 10^{13} \text{ sec.}^{-1}$ and for lead $1.9 \cdot 10^{12} \text{ sec.}^{-1}$. (The order of magnitude is that of long-wave infra-red radiation; ordinary red light has a frequency of about $4 \cdot 10^{14} \text{ sec.}^{-1}$.)

In the equation for C_p'' the only property which varies from substance to

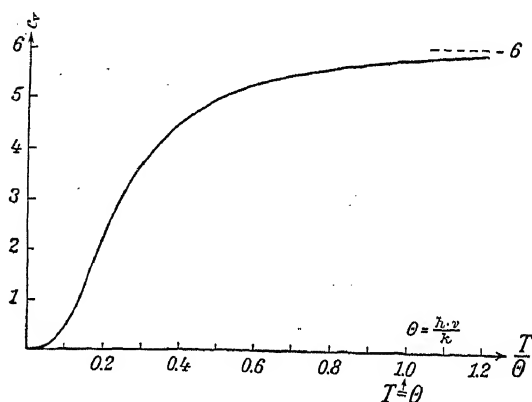


Fig. 4.— c_v of Solids as a Function of the Characteristic Temperature Θ

The values of Θ ($= h\nu/k$) for various substances are: argon, 85; lead, 88; zinc-blende, 175; silver, 215; sylvite, 230; rock-salt, 281; copper, 315; aluminium, 398; fluor spar, 474; diamond, 1860.

substance is the frequency ν and this always occurs in the combination T/ν . It follows therefore that the variation of the specific heat must be the same for all substances possessing the same number of degrees of freedom, provided that it is referred in each case to T/ν . As is shown by the curve of fig. 4, this is actually found to be the case. The variable Θ has the value $h\nu/k$ and is called the *characteristic temperature*. It characterizes thermal state in the sense that different substances are in corresponding thermal states when at their respective characteristic temperatures.

11. Mean Molecular Velocity.—Combining the equation $pV = \frac{1}{3}nm\bar{c}^2$ with the equation of state $pV = \nu RT$ we obtain

$$\frac{1}{3}nm\bar{c}^2 = \nu RT.$$

Now $nm = M$, the total mass of the gas, which can also be expressed

as $M = \nu\mu$, where ν is the number of gramme-molecules considered and μ is the molecular weight of the gas. Hence

$$\frac{1}{3} \nu \mu c^2 = R \nu T;$$

whence

$$c^2 = \frac{3RT}{\mu}.$$

This equation not only contains the relationship already derived above, namely that the absolute temperature of a gas is proportional to the mean of the squares of the velocities of the molecules; it also makes it possible to calculate a *mean molecular velocity*. According to the above equation this is inversely proportional to the square root of the molecular weight. Putting $R = 8.313 \cdot 10^7$ and $T = 273$ we have

$$\begin{aligned} c_0 &= \sqrt{3 \cdot 8.313 \cdot 10^7 \cdot 273} / \sqrt{\mu} \\ &= 260900 / \sqrt{\mu} \text{ cm. per sec.} = \frac{2609}{\sqrt{\mu}} \text{ m. per sec.} \end{aligned}$$

From this we obtain the following values at 0° C. :

	μ	Mean Velocity $\sqrt{c^2}$
Hydrogen, H_2	2	1845 m. per sec.
Oxygen, O_2	32	461 " "
Nitrogen, N_2	28	493 " "
Carbon dioxide, CO_2 ..	44	393 " "

12. Velocity Distribution.—The mean molecular velocity $c_0 = \sqrt{c^2}$ calculated in this way (the root mean square velocity) must not be confused with the arithmetic mean of the velocities. The arithmetic mean $\frac{1}{2}(m + n)$ of two numbers m and n is always smaller than the square root of the arithmetic mean of their squares, viz. $\sqrt{\frac{1}{2}(m^2 + n^2)}$. The same is also true of more than two numbers. In order to be able to calculate the difference between these means it is necessary to know in what manner the different velocities are distributed amongst the molecules. J. C. MAXWELL* was the first to discover the desired *distribution law*. Maxwell's treatment is based upon the assumption that the distribution law is independent of time, i.e. that it represents a state of dynamical equilibrium. External influences, such as addition of heat, &c., can at most change the *mean square velocity*, but the distribution of velocities about this mean is always governed by the same law. All the directions in space are taken as equivalent, so that each occurs equally often. Hence a given velocity v can result from a large number of different combinations of components. The three components of v parallel to three mutually perpendicular axes can each assume all possible values between v and 0. Maxwell investigated the mathematical probability W that a certain one of the n molecules considered should have a

* JAMES CLERK MAXWELL (1831–79), became Professor of Physics at Marischal College, Aberdeen, in 1856, was at King's College, London, from 1860 to 1865, and Professor of Physics at Cambridge from 1871. His greatest work was in connexion with the development of the kinetic theory of gases and the foundation of the electromagnetic theory of light.

velocity lying between v and $v + dv$. With the assumptions mentioned he finds, by means of the theory of probability, the value

$$W = \frac{4}{\alpha^3 \sqrt{\pi}} v^2 e^{-v^2/\alpha^2} dv,$$

In this α is a constant and W is the ratio of the number dn of the favourable cases to the total number n of possible cases, i.e. the proportion of the molecules with velocities lying between v and $v + dv$.

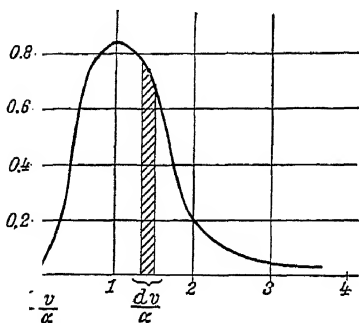


Fig. 5.—Maxwell's Law of the Distribution of Molecular Velocities. (Ordinates = $\alpha W/dv$.)

$\alpha W/dv$ as ordinates, we obtain the curve shown in fig. 5. The lengths of the ordinate of a point on the curve is a measure of the probability that a given molecule will have a velocity in the interval $1/\alpha$ cm. per sec. reckoned from v/α . The area of a strip bounded by the ordinates corresponding to the abscissæ v/α and $(v + dv)/\alpha$, the axis of abscissæ and the curve (shown shaded in the figure) is numerically equal to the probability that a certain molecule possesses a velocity between v/α and $(v + dv)/\alpha$. We notice that the curve passes through a maximum value of over 0.8 for $v/\alpha = 1$. The greatest possible value for a mathematical probability is unity; the probability is then a certainty. Hence if for $v/\alpha = 1$ the ordinate of the curve were not 0.8 but unity, this would mean that the probability of the velocity of a chosen molecule lying between α and $(\alpha + 1)$ amounts to a certainty, i.e. that all the molecules possess velocities between these limits. But the actual maximum ordinate is not unity, though it comes near to it. This means that there is a maximum probability that the velocity of any selected molecule will lie in the neighbourhood of α . Thus α represents the *most probable velocity*. Remembering now that $dn/n = W$ is the fraction of the n molecules with velocities between v and $v + dv$, and noting that the greatest part of the area between the curve and the axis of abscissæ lies in the neighbourhood of $v/\alpha = 1$, we see at once that by far the larger number of the molecules have velocities not very different from $v = \alpha$. Only a few possess velocities twice as great, still fewer possess velocities three times as great. Maxwell's *distribution law* thus shows that the assumption made tacitly above (p. 37), namely that the molecules have the same mean velocity c , is not so very seriously at variance with the actual condition of the gas.

Mean Velocity.—In order to calculate the mean velocity \bar{v} we must add together all the velocities of the n molecules and then divide by n , i.e.

$$\bar{v} = \frac{\Sigma(v dn)}{n} = \Sigma W(v) = \frac{4}{\alpha^3 \sqrt{\pi}} \Sigma \left(v^3 e^{-v^2/\alpha^2} dv \right).$$

Since v is continuously variable, the last sum becomes an integral, viz.

$$\bar{v} = \frac{4}{\alpha^3 \sqrt{\pi}} \int_0^{\infty} v^3 e^{-v^2/\alpha^2} dv.$$

Integrating we obtain
$$\bar{v} = \frac{2\alpha}{\sqrt{\pi}}.$$

Hence the *mean velocity* \bar{v} is greater than the *most probable velocity* α , as can be seen at once from the unsymmetrical shape of the area between the curve and the axis of abscissæ.

In order to find the relation between the mean velocity and the previous root mean square velocity $c_0 = \sqrt{\bar{c}^2}$, we will calculate \bar{c}^2 in the usual way, viz.

$$\bar{c}^2 = \frac{\Sigma(v^2 dn)}{\alpha^3 \sqrt{\pi}} = \frac{4}{\alpha^3 \sqrt{\pi}} \int_0^{\infty} v^4 e^{-v^2/\alpha^2} dv = \frac{3}{2} \alpha^2.$$

Hence the root mean square velocity is

$$c_0 = \sqrt{\bar{c}^2} = \alpha \sqrt{\frac{3}{2}}.$$

Care should be taken not to confuse the different velocities whose relationships are expressed in these equations.

For hydrogen we had $c_0 = 1845$ m. per sec. Hence in this case the *most probable velocity* is $\alpha = c_0 \sqrt{\frac{2}{3}} = 1506$ m. per sec., and the *mean velocity* is

$$\bar{v} = \frac{2\alpha}{\sqrt{\pi}} = c_0 \sqrt{\frac{8}{3\pi}} = 1700 \text{ m. per sec.}$$

13. Mean Free Path. Viscosity of a Gas.—In spite of their extremely high velocities, the molecules of a gas under ordinary conditions, i.e. at atmospheric pressure, do not fly very far between successive collisions. This is because of the enormous number of molecules contained in unit volume, which renders the chance of collision very great. The mean distance traversed by a molecule between successive collisions is called the *mean free path*. There are three important phenomena dependent upon the mean free path: the internal friction or viscosity, diffusion, and thermal conductivity of gases.

When one layer of a gas moves relatively to the layer next to it, the two are as it were enmeshed in each other by virtue of the molecules which fly through their common surface. Each molecule passing out of the faster moving layer into the slower brings with it a certain momentum in the direction of the former and vice versa, so that the velocity difference between the two layers tends to be neutralized. Thus the faster moving layer is retarded and the slower one accelerated (*internal friction*). A fraction of the velocity of flow is transformed into irregular molecular motion, i.e. into heat. Near the surface of a solid the influence of the molecules of the solid is so great that the surface layer of air is held quite fast when the pressure is not too high.

The existence of internal friction can be demonstrated by the following experiment. A plane circular plate is made to rotate rapidly in air and brought close to another similar plate also mounted so as to be capable of rotation. The second plate then also begins to rotate with it. The magnitude of the internal friction or viscosity is measured

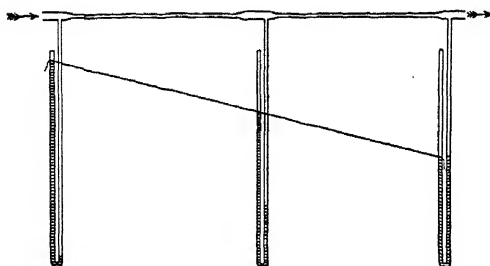


Fig. 6.—Viscosity of a Gas

by the force per unit of area between two gas layers with unit difference of velocity.

As in the case of liquids, the measurement can be carried out by means of the flow through a capillary tube (fig. 6). The fall of pressure can be measured by manometers. The observed values of the coefficient of viscosity at 0° C. are: air, 0·00018; hydrogen H_2 , 0·00008; and nitrogen N_2 , 0·0003. (For viscosity, compare Vol. I, p. 264.)

With certain simplifying assumptions the viscosity can be calculated on the basis of the kinetic theory of gases. The value obtained is

$$\eta = 0.30967 \bar{v} \lambda M,$$

where M is the mass per unit volume, \bar{v} the mean molecular velocity calculated above, and λ the mean free path. Hence

$$\lambda = \frac{\eta}{0.30967 \bar{v} M}.$$

If we divide the mean velocity \bar{v} by the mean free path λ , we obtain the number S of collisions of a given molecule per second. The following table gives a few values calculated from the formulæ.

		Mean Free Path in Cm.	Number of Collisions of Each Molecule per Second
Hydrogen	..	0·0000185	9,480,000,000
Oxygen	..	0·0000099	4,065,000,000
Nitrogen	..	0·0000160	4,760,000,000
Carbon dioxide	..	0·0000068	5,510,000,000

The greater the molecular diameter and the nearer the molecules are together, the smaller the mean free path. If n' is the number of molecules per unit volume and ρ the radius of each of them (assumed spherical), the mean free path is given by

$$\lambda = \frac{3}{16n'\pi\rho^2}.$$

Viscosity of Gas Independent of Pressure.—From the above equation it can be shown (MAXWELL, 1876) that *the internal friction of a gas is independent of the pressure*. Reduction of the pressure has two effects: on the one hand fewer molecules will pass through the common surface between two layers, but on the other hand they will be able to penetrate farther into the other layer on account of the increase of their mean free path. As far as the internal friction is concerned these opposing effects just balance each other, so that the internal friction is theoretically independent of the pressure. This result is rather surprising at first sight, but is in complete harmony with experiment. This may be shown as follows: A thin circular disc of mica is suspended from its middle point upon a thin thread so as to be able to perform torsional oscillations in its own plane. Close beneath it is fixed another plane plate and the whole arrangement is placed inside an evacuated vessel. The mica disc is set swinging (say by means of a small piece of iron wire cemented to it, which can be moved by a magnet from outside the vacuum). The motion of the disc is damped owing to the friction of the thin layer of air between it and the fixed plate. The magnitude of the damping is determined at atmospheric pressure and at reduced pressures, and is found to be always the same.

This result would seem to be at variance with the observation that in the case of moving bodies the frictional resistance of the air becomes smaller as the air pressure is reduced. The apparent contradiction is explained by the fact that in such cases there is a considerable loss of energy due to the formation of vortices. Unlike sliding friction, turbulent friction varies very much with the pressure.

The validity of the above treatment must reach a limit when the pressure becomes so small that the mean free path is of the same magnitude as the thickness of the layer between the plates. Many of the molecules will then fly from the one plate to the other without any intermediate collision, so that we can no longer speak of the sliding of one air layer over another. We should then expect that the friction would depend upon the number of collisions per second, i.e. that it would become smaller as the pressure is decreased. This is essentially the result which is actually observed at low pressures. The damping of the motion of (for example) a vibrating quartz fibre can be taken as a measure of pressure; this is the principle of the very sensitive **quartz fibre manometer** for very low pressures (KNUDSEN).

Molecular Air Pump.—GAEDÉ has made use of the viscosity of gases and of Maxwell's law in his **molecular air-pump**, the construction and operation of which may be seen from the diagram of fig. 7. A metal cylinder C rotates with high velocity in a cylindrical casing G. The space H between cylinder and casing is about 1 cm. thick and is interrupted by the ridge E. To the right and left of E are two openings *m* and *n* connected respectively with the tubes V and P. On account of the viscosity the air in the space H is carried round by the cylinder C and thus driven from V towards P. When the cylinder is rotating rapidly a manometer inserted between P and V shows a pressure difference of about 10 mm. In accordance with Maxwell's law this difference remains (approximately) constant when the air is rarified. Hence if P be connected with an ordinary air pump acting as auxiliary pump the low pressure so produced is still further reduced by the amount stated above, so that an extraordinarily high vacuum can be produced in a vessel connected with V. In this way it has

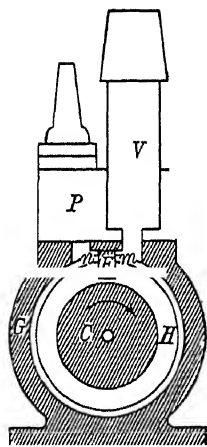


Fig. 7.—
Molecular Air Pump

been possible to attain pressures corresponding to less than 0.0000002 mm. The molecular pump does not work with the same efficiency for all gases; the most favourable are those with high molecular weights.

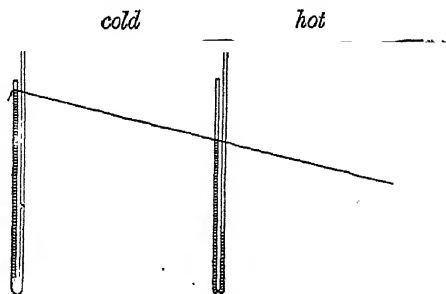


Fig. 8.—Dependence of Viscosity of a Gas upon the Temperature

Dependence of Viscosity of Gases upon Temperature.—The kinetic theory of gases also leads to the conclusion that the viscosity of a gas must increase with rise of temperature; for the greater the velocity of the molecules, the more often will they pass through the common surface between two layers of gas and hence the greater the “meshing” effect.

This can easily be proved by means of the arrangement shown in fig. 6, the second capillary being heated (fig. 8). The liquid in the middle manometer rises, because the resistance of the

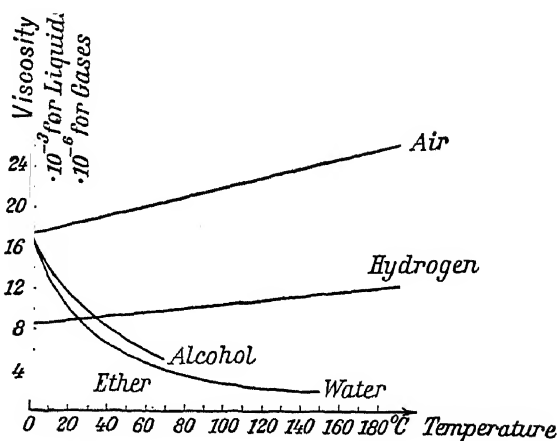


Fig. 9.—Viscosity as a Function of the Temperature

heated part becomes greater. Thus in contrast to the case of liquids the viscosity of gases increases with rise of temperature (fig. 9).

14. The Avogadro Constant.—If a gas be subjected to a very great pressure at a very low temperature, we may assume that the molecules will approach each other to the point of touching. The arrangement being imagined to be cubical, each molecule will then be enclosed in an elementary cube of edge 2ρ (ρ = molecular radius). The limiting volume of the compressed gas is thus made up of as many such elementary cubes as there are molecules present, i.e. $V = 8N\rho^3$. With the help of the equation for the mean free path given in the foregoing paragraph, we can calculate from this the important quantities ρ and N . These considerations were first put

forward in 1865 by the Austrian physicist LOSCHMIDT, who also carried out the first calculations of the corresponding numerical values. For the approximate diameter of an air molecule he obtained the value $3 \cdot 10^{-8}$ cm. He calculated the rough value $n' = 20 \cdot 10^{18}$ for the number of gas molecules in a cubic centimetre at 0° C. and atmospheric pressure. Since then this important number has been repeatedly determined by a variety of very different methods. The most reliable value is taken at present as $27 \cdot 0 \cdot 10^{18}$ (see next paragraph). There are 22,410 times more molecules in a gramme-molecule (mol) of any gas (see p. 16). The number of molecules in a gramme-molecule of a gas is known as the Avogadro constant (sometimes the Loschmidt number). Its most reliable value (determined by an electrical method) appears to be $N = 60 \cdot 6 \cdot 10^{22}$. Using this value and also that given above for the mean free path, the equation for λ (p. 50) gives the diameter of a hydrogen molecule as $2\rho = 2 \cdot 18 \cdot 10^{-8}$ cm. Since one mol of hydrogen weighs $2 \cdot 1 \cdot 0077$ gm. wt., the mass of a hydrogen atom is $1 \cdot 0077 / (60 \cdot 6 \cdot 10^{22}) = 1 \cdot 662 \cdot 10^{-24}$ gm.

2. Molecular Motion

Atomic (or Molecular) Rays.—Very special interest attaches to those phenomena which give a direct ocular demonstration of the thermal motion of molecules. In this respect the following experiments are particularly convincing.

If gas molecules are allowed to fly out of a container through a small hole into a completely evacuated space, they conserve both the direction and magnitude of their velocities and fly through in straight lines. This rectilinear motion can be demonstrated in the following way (DUNOYER, 1911, fig. 10). The source of atoms or molecules is at A (in the experiments of Dunoyer this took the form of a piece of sodium, which was allowed to evaporate *in vacuo*); the space in which it is situated is completely evacuated. B_1 and B_2 are two screens with circular openings, by means of which a conical region is left free for the flying particles. If the motion is really rectilinear, a circular deposit of sodium must be formed upon an interposed plate P. This was actually observed. Also an obstruction (e.g. a wire D) placed in the path of the atomic rays (sodium vapour is monatomic) threw a shadow upon the plate P, just as if it were placed in a beam of light. In fig. 10 the plate P is drawn at right angles to its actual position.

It was particularly desirable to investigate whether the velocity of the particles in these rays coincides with the calculated velocity.

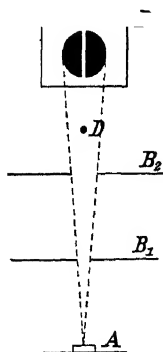


Fig. 10.—
Atomic Rays

This investigation has been carried out with success (STERN, 1920). The principle of the apparatus is shown in fig. 11. The vessel *V* is evacuated as completely as possible. Within it is the source of

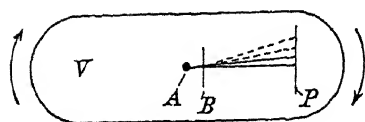


Fig. 11.—Determination of Molecular Velocity

molecules *A* (in this case this was an electrically heated platinum wire coated with silver). The gas molecules are shot out from *A* in straight lines with a mean velocity *v* corresponding to their temperature. As in fig. 10, a conical beam of atomic rays is selected by means of one

or more diaphragms. Silver atoms have the property of condensing on glass surfaces even at room temperature and hence they deposit themselves upon the glass plate *P*. The screens are so arranged that the resulting mark has the form of a line. If the whole apparatus is made to rotate rapidly about an axis through *A* perpendicular to the rays (i.e. perpendicular to the plane of the figure), the line on the glass plate *P* will be displaced somewhat in the opposite direction. For the molecules leaving *A* take a certain time to get to *P*, and during this time the plate *P* has itself moved on a small distance. Thus the rays strike the plate *P* at a different place.

If *l* is the distance between *A* and *P*, and *t* the time taken by a molecule to fly over it at velocity *v*, we have $t = l/v$. When the apparatus is rotating *v* times per second, the distance moved through by the plate in this time is $s = 2\pi lvt = 2\pi l^2v/v$. On account of the MAXWELL velocity distribution the values of *s* will be spread out over a certain range, i.e. the line on the plate will be somewhat blurred. Conversely it would be possible to calculate the velocity distribution from the intensity distribution in the line. For $v = 50 \text{ sec.}^{-1}$, $l = 10 \text{ cm.}$ $v = 500 \text{ m. per sec.}$, we have $s = 6 \text{ mm.}$

Figs. 12, 13 show the two traces (natural size) produced respectively by right-handed and left-handed rotation of the apparatus at a speed corresponding to $\nu = 45 \text{ revs. per sec.}$ The velocity value 675 m. per sec., calculated from this record and from the constants of the apparatus, is in good agreement with that to be expected from the temperature of the silver during the experiment.

These experiments demonstrate very clearly the correctness of the theories put forward in the foregoing paragraph. It has even been possible to render the paths of individual molecules visible, but these experiments cannot be discussed in this volume.

Brownian Molecular Motion.—This provides a beautiful and ocular confirmation of the kinetic theory of heat and the validity of the law of energy distribution at thermodynamical equilibrium. The English botanist BROWN called attention as early as 1827 to the motion shown under a high-power microscope by extremely small particles suspended in a liquid drop. This phenomenon is well known

to every microscopist. The motion consists of a completely irregular zig-zag displacement of the particles and a gradual progress in many small jumps. The smaller the particles, the more lively their motion. The phenomenon can easily be observed; small grains of every kind and from any source show this teeming movement. Small traces of pigments, such as bone black or carmine red, can be seen very well with high magnification. The Brownian move-



Fig. 12.—Displacement Record for Silver Atomic Rays, after Stern.

ment can be demonstrated best with the ultramicroscope in the case of ultramicroscopic particles, e.g. gold sols (Vol. I). It is scarcely observable when the diameter of the particles exceeds 0.004 mm. The motion can also be observed very beautifully in the case of extremely small particles, e.g. of tobacco smoke, suspended in the air. Fig. 13 is a microphotograph of falling oil droplets



Fig. 13.—Thermal Motion of Falling Oil Droplets, after Regener.

(REGENER). We see clearly how the smaller droplets perform the more vigorous motions.

The Brownian movements are to be explained as due to molecular motion. The molecules of the fluid medium in the immediate vicinity of a suspended particle collide with it in consequence of their thermal agitation and share their energy with it. In general the impacts on all sides of the particle will balance each other; the number of impacts per second is so immense that to observe them individually is unthinkable. The molecules have all possible velocities (p. 47), however, though according to Maxwell's law of distribution the very high values are correspondingly rare. Thus every now and then a fluid molecule strikes the particle with exceptionally high velocity, far above the mean. Hence in spite of its relatively very large mass, the particle will occasionally have such a high velocity imparted to it by a collision of this kind, that its motion will be observable under the microscope.

I. In spite of the quivering movement of the particle we observe

only a slow progress from one place to another, since the impacts are quite irregular both in time and direction and therefore balance out to a great extent. It is possible to calculate (A. EINSTEIN, 1906) how much a selected particle will be displaced in a given time τ in a radial direction from its initial position.

In this calculation the BOLTZMANN-MAXWELL law of uniform mean distribution of energy at thermodynamical equilibrium is applied to the particle. Its average kinetic energy is equal to that of a gas molecule at the same temperature, i.e. $\frac{1}{2}mc^2 = LT$. If the motion in the x -direction is observed and if the component mean square velocity in this direction is c_x^2 , then $\frac{1}{2}mc_x^2 = \frac{1}{3} \cdot \frac{1}{2}mc^2 = \frac{1}{3}LT$, since we are only dealing with *one* degree of freedom (p. 41). According to a well-tested formula of STOKES (Vol. I), the frictional resistance to which a small sphere of radius r and uniform velocity c_x is subjected in a fluid of viscosity η is $6\pi\eta rc_x$. The impacts drive the particle forwards, the frictional resistance opposes its motion. Further $LT = \frac{3}{2}RT/n$ (p. 39), where R is the universal gas constant referred to n molecules. With the assumptions mentioned it is possible to calculate (in a manner which cannot be gone into here) the mean displacement Δx of the particle in the x -direction and in the time τ . The value obtained is

$$\Delta x = \sqrt{\frac{2LT\tau}{9\pi\eta r}} = \sqrt{\frac{RT\tau}{3\pi\eta n}}.$$

It was found possible to verify this equation by quantitative experiments for various directions. Microphotographic exposures were made at short intervals of 0.1 sec. upon particles performing Brownian movements, and the plates so obtained were carefully measured. In this way it was actually found that Δx is directly proportional to the square root of the absolute temperature and of the time of observation and inversely proportional to the square root of the viscosity of the medium and also of the radius of the particle. Confirmation of the average dependence of the displacement upon $\sqrt{\tau}$ can also be found in fig. 14. The mean displacement was further found to be independent of the mass of the particle, as required by the formula. Thus the investigation led to the satisfactory conclusion that the explanation of the Brownian movement as the visible result of invisible molecular impacts is to be regarded as completely ratified. Since the equation contains as known quantities the gas constant R , the viscosity of the fluid η , the temperature T , the time interval τ , the radius r of the particle and the measured displacement Δx , it offers a direct and elegant method of *determining the number of molecules* present in the gas volume corresponding to R .

II. J. PERRIN * was the first to carry out very successful and thorough measurements upon the Brownian movement. He was able also to observe rotations in the case of larger particles; they were irregular and spasmodic, just like the translational movements. EINSTEIN has also given a formula for the magnitude of the mean rotation corresponding to the one given above, and PERRIN succeeded in verifying it completely. The formula once more contained the mean energy of a molecule corresponding to one degree of freedom. Hence the confirmation of the formula was also proof of the MAXWELL-BOLTZMANN law of equipartition of energy for rotational motions (p. 41). It also gave another independent determination of the number of molecules n .

These observations and measurements make it quite certain that the Brownian movements must be regarded as visible thermal motions.

* At Paris.

They give us a picture of the invisible molecular motions and reflect their characteristics in every detail. Brownian movements differ from molecular motions only in their extremely small velocities and their extremely small mean free paths, which are due to the great mass of the observed particles.

In this connexion the following consideration (due to PERRIN) is of interest. In fig. 14 are three diagrams formed by joining the successive positions of one and the same mastic particle at intervals of 30 sec. One of the diagrams contains 50 such positions. The figure gives a good idea of the irregularity and complexity of the path traced out by the particle. But we must bear in mind that each

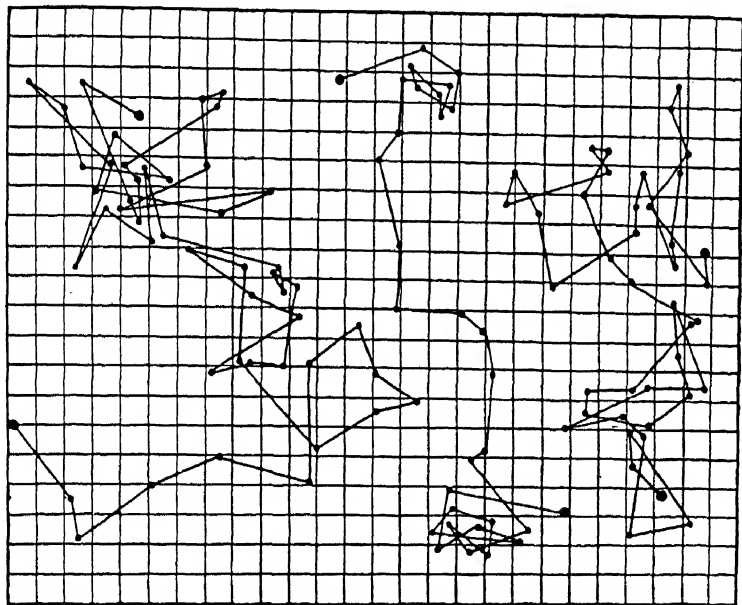


Fig. 14.—Positions of a Particle every 30 sec.

position was taken after an interval of 30 sec.; if the interval had been 1 sec. instead of 30 sec., we should have obtained a path with 30 times as many zig-zags. And if we remember that the particle is subjected to countless millions of impacts every second, we realize that the diagrams really only give a poor representation of the actual complications of the paths really traced out by the molecules.

Perhaps the most striking demonstration of the molecular kinetic nature of the Brownian movements is furnished by the following observation. When a suspension of very fine particles is left in a capillary tube to “settle out” under the influence of gravity, an equilibrium state of distribution is reached after a while. Fig. 15 shows such a distribution with a very high magnification. Fig. 16 shows cross-sections at different heights.

The observations were carried out upon the smallest particles of a mastic emulsion, obtained by dropping an alcoholic mastic solution into water and then separating the finer particles from the coarser by centrifuging. The particles had a diameter of 1μ . (This is best determined by measuring the rate of fall in water; the radius can then be calculated from STOKES'S law (p. 56).) The photographic exposures in fig. 16 were made after equilibrium had been attained, the microscope being raised by 12μ between each exposure. The figure shows a large number of particles in the lowest cross-section, whereas only 24μ higher (top section) the density of the particles has already sunk to a small fraction of that in the bottom section.

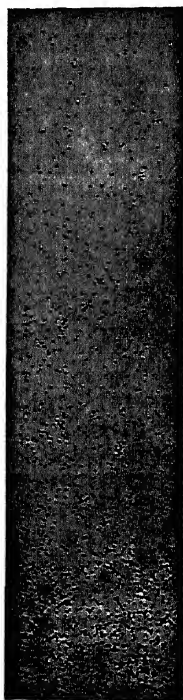


Fig. 15.—Sedimentation Equilibrium of an Emulsion as a result of Brownian Movement.

(From Eucken, *Grundriss der physikalischen Chemie*, published by Akademische Verlagsgesellschaft m.b.H., Leipzig.)

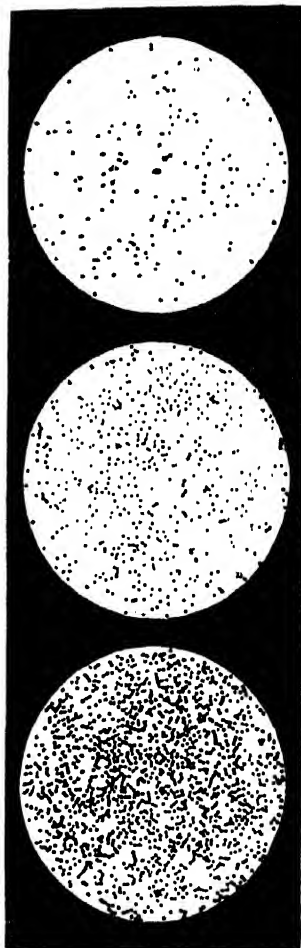


Fig. 16.—Cross-sections at Different Heights of a Suspension in Sedimentation Equilibrium. Distance between the sections 12μ .

The explanation of this is as follows: The particles suspended in a liquid behave just like the molecules of a gas, the only difference being that the particles are continually sharing energy with the molecules of the liquid by collision.

Calculation.—Consider an infinitely tall cylinder of unit cross-sectional area,

closed at the bottom and filled with a gas under the influence of gravity. Owing to gravity the paths of the molecules between successive collisions are no longer straight, but bent downwards into parabolas. If the gas was originally uniformly distributed, this curvature of the paths will cause more molecules to pass downwards through a given cross-section than upwards. In time, therefore, the number of molecules below the cross-section must increase. This means that in this region each molecule will be subjected to more collisions per second than formerly. But this causes an increased probability that the molecules will be driven up through the cross-section again as the result of a collision; for the number of impacts from below is now greater than the number from above. Thus the downward movement of the molecules due to gravity produces an opposing upward movement, the effect increasing more and more as the difference of density between different layers of the cylinder becomes greater. After a time an equilibrium state must be reached; this will be determined by the number and the weight of the individual molecules, and is characterized by a decrease of density (and therefore also of pressure) with increasing height. The weight of the molecules in any layer must be just balanced by the difference between the impacts on the lower and upper cross-sections bounding the layer. The result of this distribution is obviously expressed in the formula connecting the barometric height with the altitude (Vol. I). We can write this in the form

$$h = \frac{b_0 s'}{s_0} \log \frac{b_0}{b} = \frac{b_0 s'}{s_0} \log \frac{p_0}{p}.$$

If n and n_0 are the numbers of molecules per unit volume at the respective altitudes h and h_0 , we can put (p. 37)

$$p = gs'b = \frac{1}{3} nmc^2, \quad p_0 = gs'b_0 = \frac{1}{3} n_0 mc^2,$$

where g is the gravitational acceleration, s' the density of mercury, and b and b_0 the respective barometric heights.

As on p. 38 we write $\frac{1}{3} mc^2 = \frac{2}{3} LT = kT$, thus obtaining

$$p = gs'b = nkT, \quad p_0 = gs'b_0 = n_0 kT.$$

The density s_0 of the gas is further equal to $n_0 m$. Substituting in the barometric formula, we have

$$h = \frac{n_0 kT}{gn_0 m} \log \frac{n_0}{n},$$

or

$$n = n_0 e^{-\frac{mgh}{kT}}$$

Now by p. 40,

$$\frac{m}{k} = \frac{mN}{\frac{2}{3} LN} = \frac{\mu}{R},$$

where N is the Loschmidt number for one mol, $\mu = mN$ is the molar weight and R the universal gas constant referred to one mol. Making use of this relation, we obtain finally

$$n = n_0 e^{-\frac{\mu gh}{RT}}.$$

The number of molecules per unit volume decreases exponentially with increase of altitude according to the law

$$\log \frac{n_0}{n} = \frac{\mu gh}{RT}.$$

The particles of the mastic suspension fall in the capillary tube under the influence of gravity in exactly the same way as the molecules of the gas in the

cylinder just considered. Just as the greater density of molecules in the lower layers of the gas increases the chance of molecules being driven upwards by collision, so also in the capillary tube the probability that more particles will leave a certain layer as a result of their Brownian movement than will enter it will be greatest in those layers which are most densely populated with particles. Thus a similar equilibrium will be attained in the capillary tube to that in the gas cylinder. Now the quantities in the barometric formula which determine the distribution of the molecules are their weight mg and their mean kinetic energy $\frac{3}{2}kT$. The heavier a molecule is, the greater is the downward force upon it and hence the more rapidly will the density decrease with increase of altitude. Whereas in the case of air the barometric pressure does not fall to a half of its value until an altitude of 5400 m. is reached, the corresponding height in the case of a gas with a molecular weight 10,000 times greater would be only 0.54 m. J. Perrin was able to determine the size of his mastic particles with great accuracy by means of Stokes's law. Hence, knowing the specific gravity of mastic, it is possible to calculate the downward force upon a mastic particle, where of course the upthrust must be taken into account. This determines the value of mg in the former of the above two equations for n , in so far as it concerns this experiment. If now the numbers n_0 and n of particles be counted from the photographic exposures at the respective different heights h_0 and h , all the quantities in the equation are known except k . Hence k can be calculated; or from the second equation for n we can calculate μ and hence obtain the value of $N = \mu/m$.

We have seen that the Brownian movement provides three independent methods of determining the number of molecules in a given volume. The results of these three methods are practically identical. The latest measurements give the Avogadro constant as $N = 60.6 \cdot 10^{22}$ for the gramme-molecule or $n' = 27 \cdot 10^{18}$ for 1 cm.³ of a gas. The corresponding value of the Boltzmann constant (p. 41) is $k = 1.375 \cdot 10^{-16}$ ergs/degree and the kinetic energy of a gas molecule at the absolute temperature $T = 1^\circ$ abs., as given by the relation $k = \frac{2}{3}L$, is $L = 2.06 \cdot 10^{-16}$ ergs/degree.

3. Diffusion

1. The Brownian movement gives rise to a very important phenomenon. In mixtures where the individual molecules are capable of altering their positions in space, all substances gradually assume a distribution which, considered statistically, may be described as of perfectly random character. That is to say, all the particles in such mixtures distribute themselves after a time with the greatest possible macroscopic uniformity, provided that they are not subjected to forces of a special nature. This phenomenon is known as **diffusion**.

An example has already been given on p. 35, where it was mentioned that the denser gas bromine gradually mixes against gravity with a layer of specifically lighter air above it. In the same way the lighter gas diffuses downwards. Thus, for example, a gas jar filled with hydrogen or coal gas and closed with a cover slip may be placed downwards upon a similar jar full of air, and the cover slip removed. It can then be shown that after a few minutes in the case of coal gas

and after a fraction of a minute in the case of hydrogen the gas has moved downwards into the air in the lower cylinder, thus forming an explosive mixture there.

Similar phenomena occur also in liquids and even in solids.

If a cylinder be half filled with concentrated copper sulphate solution, and a layer of pure water poured in carefully on top, it is possible to get a quite sharp dividing surface. But if the cylinder be left to stand in a place free from vibration, the sharp dividing surface will slowly become blurred. After a few hours the blue colour shows that a part of the copper sulphate solution has risen (in spite of its greater specific gravity) about a centimetre into the water. The blurred dividing surface itself rises continuously though slowly, from which it follows that a part of the water has also passed downwards into the copper sulphate solution. After a few weeks the mixing of the two liquids is almost complete.

2. Liquids and gases also diffuse through porous dividing walls. This can be demonstrated as follows.

The bottom of a bottle is broken off and replaced by a pig's bladder, which has been soaked in water, stretched over the bottom of the bottle and bound tightly in place with string. The bottle is then filled with copper sulphate solution and closed with a bored stopper carrying a narrow glass tube, so that a part of the copper sulphate solution rises up into the tube. The bottle is then suspended in a vessel containing water. After a short time the liquid is observed to rise in the tube, i.e. there is an increase in the amount of liquid in the bottle. Water has passed from the outer vessel through the pig's bladder into the bottle. From the pale blue colour of the water in the outer vessel we conclude also that a part of the copper sulphate solution has passed out through the animal membrane. But more water has diffused into the bottle from outside than copper sulphate solution has diffused out from inside.

This process is called **osmosis**.*

3. On account of the increasing height of its column, the liquid in the inner vessel exerts an increasing pressure upon the membrane. The water must overcome this pressure in entering. Thus a stationary state is finally reached, in which the pressure has become so great that it can no longer be overcome by the water. This pressure is called the **osmotic pressure**.

It has been found possible to make membranes through which only the pure water can pass, certain solutes being unable to do so. Such membranes are said to be *semi-permeable*.

Semi-permeable membranes are prepared by filling a strong porous pot of unglazed porcelain with copper sulphate solution and placing it in a solution

* Gr., *ōsmós*, impulse, penetration. This phenomenon was discovered in 1748 by ABBÉ NOLLET (1700-70; originally abbé, then Professor of Physics at Paris from 1753, rendered valuable service in spreading the knowledge of physics by means of lectures and books; he originated the name "Leyden Jar"). It was investigated further by DUTROCHET (1776-1847, physician) in the years 1827-35. The first accurate measurements were performed, however, by PFEFFER (1845-1920, Professor of Botany at Leipzig), after he had succeeded in making resistant, semi-permeable membranes, completely impermeable to certain dissolved substances, such as cane sugar.

of potassium ferricyanide. The two liquids meet inside the porous walls and form there a precipitate of copper ferricyanide, which is permeable to water but holds back dissolved substances.

A permeable membrane must be regarded as a dividing wall penetrated by innumerable tiny channels of very different diameters, through which the molecules pass in their zig-zag motion. It is obvious that the greater the velocity and the smaller the size of the molecules, the more rapid will be their passage through the membrane; for the smaller molecules will have a greater number of possibilities of getting through, whereas the larger ones will often remain stuck. If the width of the channels is such that water molecules can pass through, but not the (usually larger) solute molecules (which generally carry along a cluster of water molecules with them), we have a semi-permeable membrane. In the same way membranes with fairly wide channels, which let through smaller molecular complexes, still hold back larger molecules or molecular complexes. Examples of such large complexes are starch powder steeped in water, dextrin, rubber, silicic acid, ferric oxide, certain dyes, proteins, &c., which can be separated by means of suitable membranes (e.g. parchment) from true molecular solutions, e.g. from associated salts or acids. In this case the process is known as *dialysis* (GRAHAM, 1862). The substances held back by the membrane are called *colloids* * (Vol. I, p. 334). The process differs in no way from osmosis, however, and there is no essential difference between colloidal solutions and "true" solutions, the molecular complexes distributed in the liquid merely being very large in the former.

Diffusion and osmosis are of the highest importance for all life processes. In a certain sense they are the basis of all life, for only by these processes can the food-stuffs provided to the body be absorbed into it. The surface area serving this purpose in the human body, i.e. the surface area of the capillaries, amounts probably to about 6000 m.².

Structures which are very similar to natural plant forms and which grow by osmosis, can be made by placing a fragment of ferrous chloride in a solution of potassium ferrocyanide or a fragment of copper sulphate, manganous sulphate or nickel nitrate in a dilute water-glass solution. Around the crystals are formed semi-permeable skins which allow the water to enter but not the salt to escape. They therefore swell up, burst at some point and then immediately form a new skin, thus growing larger and larger.

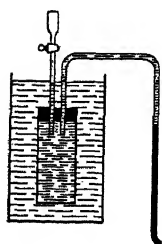


Fig. 17.—
Osmotic Pressure

4. Measurement of Osmotic Pressure.—Osmotic pressure can be measured as shown in fig. 17 with the help of an unglazed porcelain pot in whose pores semi-permeable membranes have been precipitated (see above). Through a stopper closing the pot or cell passes a U-shaped tube connected to a mercury manometer. The interior of the cell being filled with solution and the cell being placed in pure water, a rise of the manometer is observed after a short while, i.e. an increase of pressure inside the cell. Eventually the pressure inside becomes so great that it prevents any further entry of water through the walls. This final constant pressure is the *osmotic pressure* of the solution.

The following laws have been found to hold for dilute solutions:

I. The osmotic pressure is independent of the particular properties of the semi-permeable wall.

II. The osmotic pressure for a given dissolved substance at a given temperature is proportional to the concentration of the solution.

* Gr., *kólla*, glue, for which this phenomenon was first observed.

III. The osmotic pressure is proportional to the absolute temperature, the increase of the osmotic pressure per centigrade degree being $1/273 = 0.00367$ of the value measured at 0°C .

IV. Solutions containing equal numbers of gramme-molecules of different substances in equal volumes have equal osmotic pressures. Such solutions are said to be *isotonic*.

These results can be summarized as follows (VAN'T HOFF*, 1887):

The osmotic pressure of a solution is equal to the pressure which the dissolved substance would exert, if it were present as a gas in the volume occupied by the solution.

It is therefore possible by means of the osmotic pressure to determine the vapour density of a substance which cannot be brought into the vapour state, and hence also to determine the molecular weight of the dissolved substance.

As a numerical example of osmotic pressure we may take the following. The osmotic pressure of a 1 per cent sugar solution at 15°C . has been found to be 0.684 atmosphere. One litre of the solution contains 10 gm. of cane sugar ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$). The molecular weight of the solute is $\mu = 12 \cdot 12 + 22 \cdot 1 + 11 \cdot 16 = 342$, and hence there are $10/342$ gramme-molecules per litre. In the gaseous state at 0°C . and atmospheric pressure this would correspond to a volume $10 \cdot 22.4/342$ litre (p. 16), or at 15°C . the volume $(10 \cdot 22.4/342) \cdot 288/273 = 0.691$ litre. If this volume were to expand to 1 litre, its pressure would fall to 0.691 atmosphere. This is in very good agreement with the observed osmotic pressure.

In this calculation the molecular weight of cane sugar was taken as known. If it had been unknown, it could have been calculated from the observed osmotic pressure.

The laws mentioned above only hold for dilute solutions and also only for those solutions which do not conduct an electric current (Vol. III), i.e. mainly for organic substances like cane sugar, alcohols, and the like.

5. The phenomena of diffusion can be observed particularly easily in the case of gases, especially if suitable permeable membranes be used (e.g. porous porcelain cylinders).†

The velocity of diffusion is found to be different for different gases, being greatest for gases of low molecular weight.

The **velocity of diffusion** is measured by the amount of gas passing in unit time through unit area of the membrane.

The difference of the velocities of diffusion of different gases can be demonstrated by means of the following experiment (fig. 18). A porous porcelain cell, such as is used in galvanic elements, is closed by a bored stopper through which passes a long glass tube. The lower end of this tube dips into water. Over the porous cell is hung a glass beaker. Coal gas or better hydrogen is now allowed to enter the beaker from below. It diffuses with such velocity through the porous walls that a rapid stream of bubbles issues from the lower end of the glass tube. The beaker is then removed. The porous cell is now surrounded by air, but contains inside it a mixture of air and gas. The gas once more diffuses so rapidly through the porous walls that the water closing the tube below rises considerably.

Carbon dioxide diffuses more slowly than air. Hence if a porous cell be dipped in a vessel filled with carbon dioxide (as in fig. 19), the water first rises up the

* JACOBUS HENDRIK VAN'T HOFF, born at Rotterdam in 1852, Professor of Theoretical Chemistry in Amsterdam and then in Berlin from 1899 to his death in 1911.

† In this case the process is sometimes called *transfusion*.

tube. The beaker being removed, the rapid diffusion of air into the cell causes a vigorous stream of bubbles to issue from the lower end of the tube.

The phenomenon finds practical application for the detection of light (and mostly dangerously combustible) gases, e.g. to detect the presence of hydrogen in airship or balloon gondolas. The diffusion of gases is also made use of in certain air pumps (GAEDÉ) of extreme efficiency (Vol. I).

The above experiments show that at a given temperature the more rapidly moving molecules (p. 47) of the lighter gas make their way more quickly than the slower molecules of the heavier gas through the pores of the porcelain pot. We should therefore expect the velocity of diffusion to be proportional to the molecular velocity, i.e. inversely as the square root of the molecular mass. This is actually so for narrow pores.

An interesting consequence of the thermal motion of molecules is the phenomenon of the different velocities of diffusion of one and the same gas at different

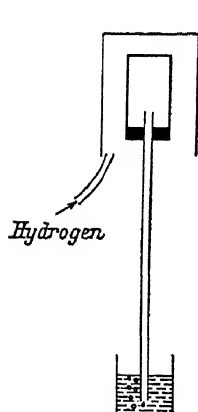


Fig. 18

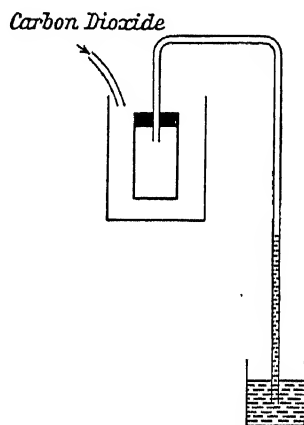


Fig. 19

Diffusion of Gases through Porous Wall

temperatures. This can be shown very beautifully by a method similar to that shown in fig. 18, the air inside the cell being heated (e.g. by means of a glow lamp with leads passing air-tight through the stopper) instead of a different gas being used outside. It is then found that at equilibrium the pressures inside and outside are not equal, but that there is a constant excess pressure inside the cell. So long as the temperature within the cell is higher than outside, bubbles of air issue from the glass tube into the water. If the tube be closed, the pressure rises until the number of molecules entering the cell through the pores is equal to the number leaving. If n_1 and n_2 are the numbers of molecules per cm.³ inside and outside respectively, then at equilibrium we have

$$n_1 v_1 = n_2 v_2,$$

where v_1 and v_2 are the corresponding velocities. But

$$p_1 : p_2 = n_1 v_1^2 : n_2 v_2^2,$$

and hence at equilibrium

$$p_1 : p_2 = v_1 : v_2 = \sqrt{T_1} : \sqrt{T_2}.$$

This relationship has actually been verified (KNUDSEN).

CHAPTER III

Change of State

1. Solids, Liquids and Gases

In general when heat is added to a solid it becomes liquid at a certain temperature (the **melting-point**); similarly the liquid becomes gaseous at a certain higher temperature (the **boiling-point**). The case can also arise, however, in which a solid passes directly into the gaseous state (**sublimation**). Conversely a gas will in general become liquid at a certain temperature (the **liquefaction-point**) when heat is withdrawn from it; and a liquid will become solid at a certain temperature (the **solidification- or freezing-point**). For a **pure substance**, i.e. one consisting only of one kind of molecule, the melting-point and the solidification-point are identical, as are also the boiling-point and liquefaction-point.

In solids the molecules have no translational motion, but must be imagined as vibrating about mean equilibrium positions (cf. § 1, 6, p. 41). They hold each other in these equilibrium positions by virtue of their mutual attractive and repulsive molecular forces. Addition of heat increases the energy of vibration, i.e. increases the amplitude. The molecules require more space: the body expands. When the melting-point is reached, the motion becomes partly translational; the molecules are then able to leave their places.

In liquids, on the contrary, the molecules are in rotational and translational motion, which, however, is not so great that they can overcome their mutual attractions. The molecules of a liquid can indeed change places under the influence of small forces; but in consequence of their dense packing and their frequent collisions they only progress slowly by thermal agitation. The assumption of translational motion is necessitated by the phenomenon of *diffusion* (p. 60); for liquids also diffuse through one another, though very slowly in comparison with gases. Diffusion has also been demonstrated in the case of solids, e.g. gold into lead, but it only becomes perceptible after years. From this it follows that even in solids a certain very small proportion of the molecules are in translational motion. These are the molecules which happen to have been knocked out of their equilibrium positions by very energetic impacts.

In addition the **evaporation of liquids** (and also of many solids)

necessitates the assumption of a translational motion. If the molecules moving in the immediate vicinity of the free surface once break through it and pass out of the sphere of attraction of their neighbours, they will fly off as gas molecules into the space above the liquid. If we imagine the space to be closed, it will gradually be filled with more and more gas molecules, which will collide with each other and with the boundary walls and thus be partly driven back into the liquid and caught by it. After a time an equilibrium state is reached, in which the number of molecules turned back into the liquid is equal to the number flying out. This is known as the *saturation state*. Addition of heat, i.e. rise of temperature, increases the velocity and hence also the kinetic energy of the liquid molecules. This is the reason why the number flying clear of the liquid becomes greater: the equilibrium is displaced towards the side of the vapour. Finally, when the velocity of the molecules has been increased by addition of heat until they can overcome the whole of the pressure of the air above the liquid, the liquid *boils*.

In the change of a substance from the liquid to the solid state or from the liquid to the gaseous state there are often inhibitions, reminiscent of states of unstable equilibrium.

Thus a liquid in a perfectly clean vessel protected from vibration can often be cooled down far below its normal solidification point without becoming solid (**supercooling**). With careful cooling, water can be taken down to a temperature of -10°C . and lower in a clean vessel. But if the water is disturbed by means of a sharp blow upon the vessel with some hard implement, freezing suddenly sets in and a thermometer dipping in the liquid (see fig. 2, p. 69) rises to 0°C . (the normal freezing-point).

The solutions of certain salts show a behaviour similar to supercooling. For instance 100 gm. water dissolve approximately 50 gm. of sodium sulphate (Glauber's salt) at 33°C ., and only about 13 gm. at 15°C . But if a solution saturated at 33°C . be cooled without vibration, the excess (37 gm.) of salt remains in solution (**super-saturation**). If now the cooled solution be disturbed or a fragment of the solid salt allowed to come in contact with it, the whole excess of salt crystallizes out with simultaneous rise of temperature. Sodium thiosulphate also shows the same behaviour; it dissolves at 48°C . in its water of crystallization, but when cooled again to room temperature without vibration it remains liquid.

By heating water carefully in a clean vessel it is possible to raise its temperature several degrees above the normal boiling-point (100°C .) without its beginning to boil (**superheating** or **delayed boiling**). Also in this case a sharp disturbance causes boiling to set in with great (often explosive) vigour, the thermometer falling to 100°C . The so-called "bumping" during slow boiling of water in glass vessels

is due to superheating of this kind and its sudden disappearance.

Supercooling and superheating can be avoided by placing small solid bodies in the liquid, especially if they have sharp edges, e.g. fragments of glass or metal shavings. Their influence is probably to be explained as due to a change of surface tension. Superheating and bumping can be most effectively prevented by the addition of small porous objects, such as pieces of filter paper, pumice stone or tile. They remain effective so long as they are still able to release air from their pores. A slight chemical development of gas within the liquid is also a certain means of preventing delayed boiling. Very small air bubbles present in or introduced into the liquid favour evaporation by forming "nuclei" for the vapour bubbles. Hence water which has been freed to a great extent from air under the pump or by long boiling exhibits the phenomenon of superheating in the greatest degree.

Gases can remain gaseous at temperatures below their normal boiling-point or **condensation-point**. Sudden condensation is then brought about by blowing in fine dust particles. These form "*condensation nuclei*" by adsorbing (Vol. I) the gas molecules upon their surface and thus instigating liquefaction. This is the reason why fogs are more easily formed in the neighbourhood of cities with smoking chimneys than in country districts.

2. The Processes of Melting and Solidification

1. **Determination of the Melting-point.**—For this purpose the solid is placed in a small thin-walled tube which is then fastened to the glass of a thermometer, the whole being finally brought into a liquid bath. The bath is heated up gradually and the temperature read off on the thermometer at the moment when the substance in the tube becomes liquid.

This method is only applicable for bodies whose melting-points are not too high. Determinations of higher melting-points and indeed all measurements of high temperatures are made by other methods, which cannot be discussed until Vol. III.

For a few very accurately known melting-points see p. 6. Further constants are to be found in Table I (p. 289).

Melting- and solidification-points can also be determined from the cooling curve (see p. 71).

2. **Change of Volume accompanying Solidification.**—For most substances there is an increase of volume during melting and a decrease during solidification. This is the explanation of the formation of deep holes in the middle of the surface of molten wax, molten lead, and most other molten substances when they are cast in a mould. Closed cavities in castings are also due to the same cause. For this reason the moulds are provided with extensions where the molten substance is poured in. These necks are also filled, so that during solidification the liquid in them may flow into the mould proper and keep it quite full.

A few substances exhibit quite the opposite behaviour: they expand during solidification. This is particularly pronounced in the case of water, the volume increasing by 9 per cent during freezing to ice. This is the cause of the bursting power of freezing water, the weathering of rocks and stones (into whose cracks water penetrates, freezes and thus forces the sides apart), the bursting of water-pipes and motor-car radiators, &c. The pressure exerted by freezing water is so great that if a hollow cast-iron sphere, 1 cm. thick, is filled with water and closed tightly with a screw, it is burst when the water freezes. Cast iron and bismuth also expand on solidification. (For the application of this type of expansion in the *ice calorimeter* see below.)

There is a very great increase of volume during the change of a liquid to the gaseous state, i.e. during evaporation. Thus, for example, water vapour at 100°C . and atmospheric pressure occupies about 1700 times the volume of the same mass of liquid water under the same conditions.

3. Latent Heat of Fusion.—There is no rise of temperature while a solid is being melted by addition of heat; the whole of the heat added is used up in changing the state of aggregation of the substance.

The quantity of heat in cal. (Cal.) required to change 1 gm. (1 kg.) of a substance from the solid to the liquid state without change of temperature is called the **latent heat of fusion** of the substance.

1 kg. of water at 100°C . is mixed with 1 kg. of ice at 0°C . in a thin-walled vessel of small heat capacity. After all the ice has been melted, the temperature of the mixture is found to be 10°C . The 1 kg. of water gave up 90 Cal. during its fall of temperature from 100°C . to 10°C . Of this 10 Cal. were used up in raising the temperature of the melted ice from 0°C . to 10°C . Hence the apparently lost 80 Cal. must have been required to change the 1 kg. of ice into water at constant temperature. The latent heat of fusion of ice* is therefore 80 (more accurately, 79.67) Cal./kg. or cal./gm.

Water possesses the highest latent heat of fusion of all substances. Amongst others may be mentioned: lead, 6; silver, 21; and mercury, 3 cal./gm. For other values see Table I.

The known latent heat of fusion of ice is used as follows for the determination of specific heats. A hole is made in a block of ice and is provided with a well-fitting cover also made of ice. The body under investigation is heated up to a known temperature and then placed in the hole, which has been previously thoroughly dried, and the ice cover is placed over it. Time is then allowed for the body to cool down to 0°C ., when the hole is opened and the mass of ice melted determined by weighing. From this it is possible to calculate the quantity of heat given up by the body, and hence also its specific heat (BLACK, about 1760).

* DELUC discovered in 1754 that heat disappeared (became latent) during the melting of ice. J. BLACK was the first to determine the latent heat of fusion accurately. He obtained the value 79.5, WILCKE having found the value 72 at about the same time.

In the **Bunsen ice calorimeter** use is made of the fact that ice contracts on melting. Actually 1 gm. of ice at 0° occupies a volume greater by 0.0917 cm.^3 than that of 1 gm. of water at the same temperature. The Bunsen ice calorimeter (fig. 1) consists of a bent glass tube AB into whose wider limb A is fused a narrower tube closed at the bottom. The body to be investigated calorimetrically is placed in this latter tube. On to the narrower limb B is joined a horizontal capillary D, which has been previously accurately calibrated. The wider limb A is filled with pure water, which is closed below by mercury. The mercury also fills the limb B and extends into the capillary D. The whole apparatus, with the exception of the capillary, is placed in a vessel of melting ice, so that its temperature is maintained always at 0° C.

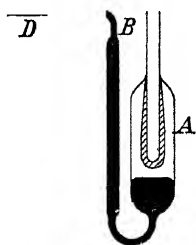


Fig. 1.—Bunsen Ice Calorimeter

Ethyl ether or solid carbon dioxide is first evaporated in the fused-in tube, thus causing an ice layer to be formed around it. The freezing water expands during the process and drives the mercury thread along the capillary. A known mass of the substance to be investigated is then heated up to a known temperature and placed in the tube; or alternatively the process to be investigated (e.g. a chemical reaction) is allowed to take place there. From the distance which the mercury moves back along the capillary it is possible then to deduce the mass of ice melted and hence the quantity of heat given up. Once the apparatus is prepared, very accurate calorimetric measurements can be carried out with it in a short time and with small quantities of substance.

In passing from the liquid to the solid state a substance gives up its latent heat of fusion again (**heat of solidification**). From this it follows that in general a liquid can be made to solidify by withdrawing heat from it, i.e. by cooling.

If a body is made to pass from the liquid to the solid state without withdrawal of heat, a *rise of temperature* occurs. Thus the temperature of supercooled water rises from -10° C. to 0° C. when freezing is started by shock.

This behaviour can be shown conveniently with the help of the *freezing thermometer* shown in fig. 2. This consists of an ordinary thermometer surrounded by a glass vessel partly filled with pure boiled water.

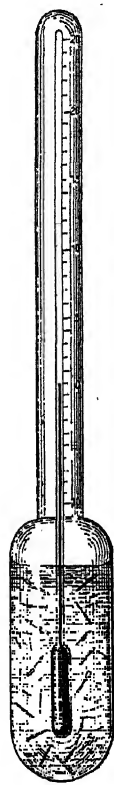


Fig. 2.—Freezing Thermometer

4. Heat of Solution.—Heat is always used up in melting a solid. The same is usually true in the case where a salt is brought into the liquid state by solution in water; the temperature usually falls while the salt is dissolving. This effect is particularly striking in the solution of salt-petre or sodium thiosulphate in water.

The quantity of heat required for solution is called the **heat of solution**.

When crystals are deposited from a supersaturated solution of Glauber's

salt or sodium thiosulphate (p. 66) there is a marked rise of temperature, analogous to that due to heat of solidification.

5. Freezing Mixtures.—When equal parts of finely powdered ice and common salt are mixed, the temperature falls to -20°C . This large fall is due to the fact that brine (salt solution) is formed (see below); both constituents of the mixture pass into the liquid state, thus requiring a large quantity of heat, which they draw from the surroundings.

6. Melting-point or Freezing-point of Solutions.—Solutions freeze at a lower temperature than the pure solvent, the lowering of the freezing-point being proportional to the concentration of the dissolved substance, provided this is not too great. The lowering produced by 1 gm. of the solute in 100 gm. of the solvent is called the **specific depression of the freezing-point**.

RAOULT showed in 1886 that the specific depression of the freezing-point of a solvent is inversely proportional to the molecular weight of the dissolved substance. Hence we can express the law of freezing-point depression as follows.

The depression of the freezing-point is proportional to the number of grammes-molecules of the solute dissolved in unit volume, and is independent of the particular nature of the solute.

The product of the specific depression θ and the molecular weight μ of the solute is therefore a constant C of the solvent, independent of the nature of the solute, i.e.

$$\mu\theta = C.$$

The value of C for water is 18.3, for acetic acid 39, and for benzene 51.

The depression of the freezing-point provides the chemist with an important method of determining the molecular weight of a substance. For example, if 1 gm. of cane sugar is dissolved in 100 gm. of water, the observed depression of the freezing-point is $\theta = 0.054^{\circ}\text{C}$. Therefore the molecular weight of cane sugar is $\mu = C/\theta = 18.3/0.054 = 339$ (cf. p. 63). (**Cryoscopic** * method of molecular weight determination.)

When the concentration of the dissolved substance becomes greater, the conditions are more complicated, since it is no longer possible to distinguish between solvent and solute. This case arises, for example, in alloys. Figs. 3 and 4 show the behaviour of a copper-gold alloy and an iron-carbon solution. The melting-points have been plotted as ordinates and the composition of the systems as abscissæ. The upper curve gives the melting-points for the corresponding compositions. The complicated behaviour represented by the lower curves (see below) cannot be discussed here.

As can be seen from the figures, the *melting-point of a metallic alloy* is in general lower than would be expected from the proportions of the constituents. It often lies lower than the melting-point of the more easily fusible constituent of the alloy. Thus, for example, the melting-point of an alloy of equal parts of tin and lead (soft solder)

* Gr., *kryos*, frost, ice; and *skopéin*, to look at.

is at 200°C . Wood's metal, consisting of an alloy of 1 part of cadmium, 1 part of tin, 2 parts of lead, and 4 parts of bismuth, melts as low as 68°C .; hence it becomes liquid in boiling water, whereas none of its

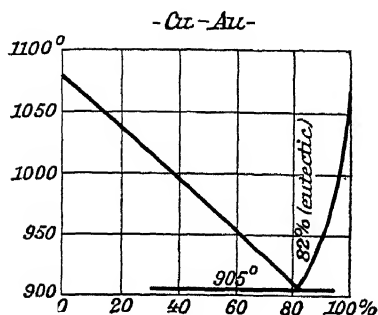


Fig. 3.—Melting-point Diagram for the System Copper-Gold

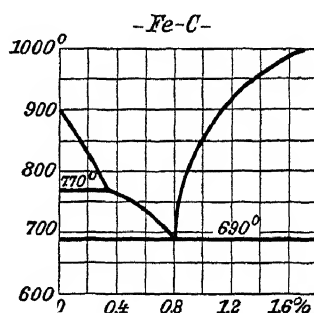


Fig. 4.—Melting-point Diagram for the System Iron-Carbon

constituents has a melting-point below 200°C . An alloy of equal parts of sodium and potassium is liquid at ordinary temperature, although each of these metals alone is solid under the same conditions.

7. Determination of Melting- and Freezing-points from the Cooling Curve.—

When a liquid melt is allowed to cool, its temperature falls continuously. Eventually the freezing-point is reached and the substance begins to separate out in solid form. The temperature now remains constant until the whole has become solid. It then begins to fall once more (fig. 5). In this way the solidification temperature can be determined very accurately by means of the curve obtained from continuous temperature measurements. In general, solutions show no such period of constant temperature during freezing. This is due to the fact that often when a solution freezes only pure solvent is deposited (e.g. pure, salt-free ice from sea water); the remaining liquid therefore becomes more and more concentrated and shows a lower and lower freezing-point (see above). The horizontal lines in figs. 3 and 4 give the temperatures at which the whole mixture finally becomes solid. If, however, the solute and solvent are deposited in the same proportion as in the liquid, then the concentration and freezing-point of the residual melt remains constant. Hence such a solution melts and solidifies just like a pure substance. A mixture of this sort is called an eutectic. For easily appreciated reasons its composition is given by the lowest point of the melting-point diagram (see figs. 3 and 4). In the case where one of the components is *water*, we also speak of *cryohydrates*.

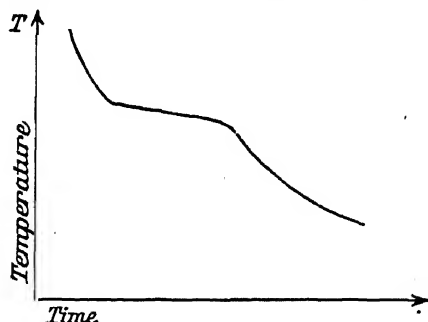


Fig. 5.—Cooling Curve for the Solidification of a Pure Substance

8. Dependence of Melting-point upon Pressure.—The melting-point of a substance is not an absolute constant; it varies with the

pressure to which the substance is subjected. Those substances which contract on solidification have their melting-points raised by increase of pressure (§ 15, p. 153).

Under high pressure they melt at a higher temperature than under lower pressure; for example, mercury under 15,000 atm. pressure does not melt until $+10^{\circ}\text{C.}$, whereas under 1 atm. it melts at -39°C. On the contrary, those substances which expand on freezing have their melting-points depressed by increase of pressure (the brothers JAMES and WILLIAM THOMSON, 1850). For instance, the melting-point of ice is depressed by 0.0075°C. for each 1 atm. increase of pressure.

Thus water freezes at a temperature below 0°C. when under great pressure. It is possible to liquefy pieces of ice by means of high pressure in a steel cylinder. When the cylinder is opened the various pieces of ice are found to have formed one uniform mass (TYNDALL),* since the pressure is thereby released and the melting-point returns to the normal (regelation†).

The plasticity of ice and the formation and flow of glaciers can be explained (TYNDALL, HELMHOLTZ) by the fact that upper masses of ice and snow exert such a great pressure upon the lower ice layers that a partial melting takes place. The resulting water flows into the cracks and at once freezes again. This explanation is not a sufficient one in all cases, however; for in very cold lands the observed temperatures inside glaciers are so far below the normal freezing-point that the actual pressures are not great enough to cause melting. Thus for example the internal temperature of the glaciers in Greenland is between -15°C. and -16°C. or sometimes much lower (see Vol. I, p. 267). The ice underneath the blades of skates is subjected to the pressure of the skater's weight; it therefore melts and thus facilitates gliding.

If a block of ice be placed in a fork-shaped stand and a piece of thin steel wire hung over it, with weights (each about 10 kg. wt.) at the ends, the wire will cut deeply into the block owing to the melting of the ice immediately underneath it. The water so formed flows round the wire and freezes once more to ice above it; thus after the wire has passed right through, the block of ice is still whole and solid.

The change of volume on solidification and the change of the melting-point are connected with the latent heat of fusion by the following equation (for the method of proving which see p. 143):

$$\delta = 0.0242 \frac{(V_1 - V_2)T}{L} \text{degrees/atm.,}$$

* JOHN TYNDALL (1820-93), studied from 1848 to 1850 at Marburg (under Bunsen) and in 1851 at Berlin (under Magnus); from 1853 onwards Professor of Physics at the Royal Institution and at the School of Mines in London as the successor of MICHAEL FARADAY (Vol. III); celebrated in his day on account of his brilliant skill as an experimenter and his fascinatingly written popular works upon various physical themes; he was also a prominent supporter of mountaineering sport in the Alps.

† Lat., *regelare*, to freeze again. The phenomenon of regelation was discovered by MICHAEL FARADAY in 1850. The name is due to TYNDALL.

δ being the elevation of the melting-point for one atmosphere increase of pressure, V_1 and V_2 the volumes of 1 gm. of the substance in the liquid and the solid states respectively, T the absolute temperature and L the latent heat of fusion in calories per gramme.

The changes of melting-point caused by changes of pressure are so small that those corresponding to variations of *atmospheric pressure* are always negligible.

3. The Processes Involved in Vaporization

1. Determination of the Boiling-point.—In determining boiling-points with a thermometer the question arises as to whether this should be placed in the boiling liquid or in the vapour from it. It is found that the vapour always has the same temperature, provided that it can escape freely; but on account of superheating (see above) a thermometer placed in the liquid often shows very considerable variations. Hence boiling-points may only be determined with the thermometer in the vapour. Examples of actual values: mercury, 356.7°C .; alcohol, 78.3°C .; ether, 34.6°C .; liquid air, -193°C . For further numerical data see p. 6 and Table I (p. 289).

2. Latent Heat of Vaporization.—Heat is required to bring a body from the liquid into the gaseous state. This is illustrated by the fact that a flame beneath boiling water supplies heat continuously to it without causing the temperature to rise above 100°C . Thus when the temperature of a liquid (we refer here only to a single pure liquid substance) has reached the boiling-point, it does not rise any more when further heat is supplied, but remains constant. The heat is then used up in transforming the liquid into vapour at the same temperature.

The quantity of heat in gramme-calories which is required in order to vaporize 1 gm. of a liquid at constant temperature is called the **latent heat of vaporization** of the substance. A numerically identical value is obtained by expressing the quantity of heat in kilogram-calories and taking 1 kg. as the unit of mass. When the vapour condenses, the same quantity of heat is given up again (**heat of condensation**).

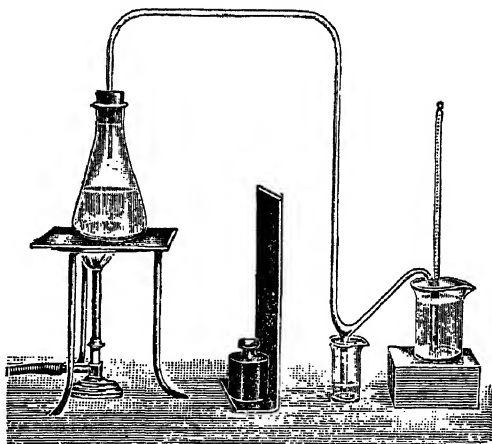


Fig. 6.—Determination of the Latent Heat of Steam

Determination of the Latent Heat of Vaporization of Water.—By means of the arrangement shown in fig. 6 the vapour from boiling water is led into a weighed quantity m_1 gm. of cold water at temperature t_1° C. The branch tube at the lowest point of the bent tube dips in a vessel of hot water and receives the water which has already condensed. Suppose that the temperature of the originally cold water rises to t_2° C. on account of the steam passing into and condensing in it, and that the final mass of water (obtained by re-weighing) is m_2 gm. Then the mass of steam condensed in the calorimeter vessel is $(m_2 - m_1)$ gm. The corresponding latent heat has been given up to the calorimeter and contents as *heat of condensation*. Let the latent heat of vaporization be x cal. Then $(m_2 - m_1)x$ cal. is the quantity of heat given up by the steam in changing to liquid water at 100° C. This condensed water then gave up $(m_2 - m_1)(100 - t_2)$ cal. in cooling from 100° C. to t_2° C. The calorimeter and original contents were heated up through $(t_2 - t_1)^\circ$ C., i.e. absorbed the quantity of heat $m_1(t_2 - t_1)$ cal. We have therefore $(m_2 - m_1)x + (m_2 - m_1)(100 - t_2) = m_1(t_2 - t_1)$. Hence

$$x = \frac{m_1(t_2 - t_1)}{m_2 - m_1} - 100 + t_2.$$

Example.—The masses of water in the calorimeter before and after passing in the steam were $m_1 = 501$ gm. and $m_2 = 504.3$ gm. respectively. The temperature rose from 16.45° C. to 20.53° C. Then

$$x = \frac{501(20.53 - 16.45)}{504.3 - 501} - 100 + 20.53 = \frac{501 \cdot 4.08}{3.3} - 79.5 = 540 \text{ cal./gm.}$$

The accurate value of the latent heat of vaporization of water is 539.1 cal. per gm. (Table I.) The greater part of this is used up in changing the state of aggregation, a relatively small fraction (amounting to 40.3 cal. per gm.) going to perform the work required to bring about the increase of volume against atmospheric pressure (p. 33). The total latent heat of vaporization is thus composed of two parts: (i) the actual *internal* latent heat of vaporization which brings about the molecular process of evaporation, i.e. the overcoming of the forces of cohesion, and (ii) the *external* latent heat of vaporization, which goes to perform the external work.

Even at ordinary temperature a liquid passes into the state of vapour. This vaporization takes place only at the free surface and is called **evaporation** (p. 81). Heat is also required for evaporation. Hence the temperature of water in an open vessel is always somewhat lower than that of the air.

In many parts of the world drinking water is kept cool by storing it in porous vessels through which it percolates slowly. The vessel being placed in the fresh air, the water evaporates to some extent on the outer surface and the necessary quantity of heat is drawn from the surroundings, including the water in the vessel, which is thereby cooled. On a hot summer day the cooling effect of sprinkling water is well known. Liquids which evaporate rapidly at ordinary temperature can give rise to a very great temperature fall. The rate of evaporation of ether from a vessel is accelerated by blowing in air, and the cold produced may be sufficient to cause the vessel to freeze tightly on to the table, if the latter be wet. Considerable reduction of temperature renders the tissue of animal bodies insensitve. To produce anaesthesia during surgical operations the skin is often sprayed with ether or better with the even more rapidly evaporating and more effectively cooling methyl chloride.

For the application in hygrometers and psychrometers see § 5, p. 86.

3. **Effect of Pressure on the Boiling-point.**—The boiling-points given on p. 6 and in Table I refer to the case in which the boiling liquid is subjected to a pressure of one atmosphere. The values are altered by increase or decrease of pressure.

The boiling-point of water under increased pressures can be determined, for example, in PAPIN'S * pot (fig. 7). This is a pot made of stout copper sheet and tightly closed with a cover secured with screws. The cover carries a safety valve, a manometer, and an iron tube closed at its lower end. This tube is filled with mercury, into which dips a thermometer to determine the temperature of the interior. The pot is partially filled with

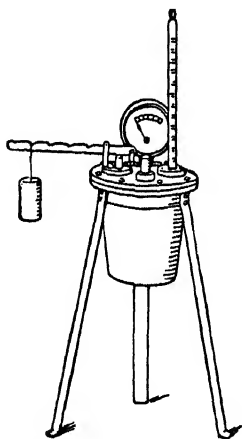


Fig. 7.—Papin's Pot

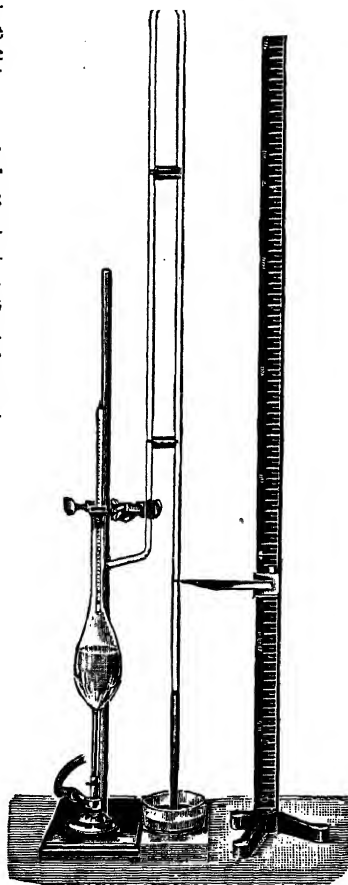


Fig. 8.—Boiling-point under Reduced Pressure

water, closed and heated with a flame. The steam is unable to escape; it therefore exerts a great pressure upon the whole interior of the pot, including the water. This pressure can be read off upon the manometer. There is a simultaneous rise of the boiling-point of the water as indicated by the thermometer. The following table gives the observed boiling-points at different pressures.

Pressure in atmospheres	1	2	3	4	5
Boiling-point in °C. . .	100	121	134	144	152

* DENIS PAPIN (1647–1712), from 1672 assistant to HUYGENS, from 1688 Professor at Magdeburg. In 1681 he invented the steam cooking pot, in which food is cooked at temperatures above the normal boiling-point (100° C.). He also invented the safety valve, the modern design of which is still essentially the same as that of PAPIN. He constructed the first—though very imperfect—steam-engine in the year 1690.

The boiling-point of water under reduced pressure may be determined with the apparatus shown in fig. 8. A round-bottomed flask partially filled with water has a thermometer inserted air-tight in its neck. The neck is also provided with a side tube which is bent upwards and then downwards again as in the figure. The vertical downward limb is about 1 m. long and its lower end dips in a vessel containing mercury. When the water is brought to the boil by means of a flame beneath it, the steam developed drives the air out of the tube. The observed boiling-point is 100°C . The flame is then removed or turned low. The temperature within the flask sinks, but in spite of this the water goes on boiling. At the same time the mercury rises up the tube. The boiling-points are read off

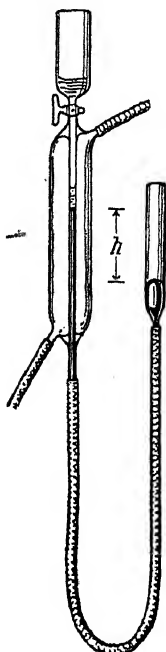


Fig. 9.—Vapour Pressure of Water

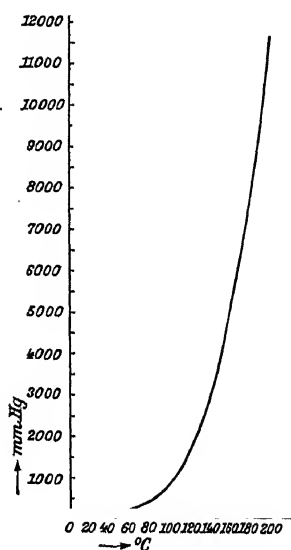


Fig. 10.—Vapour-pressure Curve for Water

on the thermometer and the corresponding levels of the mercury noted. The pressure is in each case equal to the barometric pressure minus the height of the mercury column in the tube. The following table gives the observed results.

Pressure in mm. of mercury	760	526	355	233	149	92	55	32
Boiling - point of water in $^{\circ}\text{C}$. ..	100	90	80	70	60	50	40	30

4. Vapour Pressure.—By means of the arrangement shown in fig. 9 it can be shown that water vapour exerts a measurable pressure even at low temperatures.

A glass tube about 1 m. long is provided with a tap, above which the tube widens to a small vessel. The lower end of the tube is connected by means of

thick-walled rubber tubing with a levelling vessel. The tube is also surrounded by a wider glass jacket through which water at known temperature can be passed. In this way the whole of the inner tube is heated or cooled to a known temperature. By filling the levelling vessel and the rubber tubing with mercury, raising the former till the whole glass tube is filled with mercury, closing the tap and lowering the levelling vessel more than 760 mm., a vacuum is produced below the tap. When now a little water is allowed to enter this vacuum from the wider part of the tube above the tap, there is a sudden vaporization and the mercury sinks in the glass tube by an amount equal to the vapour pressure of the water.

The vapour pressure is equal to the difference between the barometric height and the height h between the two mercury levels (see figure). The following table gives the observed results.

Temperature in °C. ..	5	10	15	20	25	30
Vapour pressure in mm. of mercury	6.5	9.1	12.7	17.4	23.8	31.8

A general idea of the relations between vapour pressure and temperature is best obtained from a graphical representation in which the temperatures are plotted as abscissæ and the corresponding vapour pressures as ordinates (fig. 10). The numerical data for water are given in Table IV (pp. 290, 291). It is seen from the curve of fig. 10 that with rise of temperature the vapour pressure increases at first slowly and then more and more rapidly. The boiling-point of water at any pressure can be obtained from the curve and Table IV.

The boiling-point under a given pressure is the temperature at which the vapour pressure becomes equal to that pressure.

Thus, for example, the boiling-point of water under a pressure of 1500 mm. of mercury is 120° C.; for at this temperature the vapour pressure is equal to 1500 mm. of mercury.

The vapour-pressure curve for water is shown again in fig. 11 for temperatures between -10° C. and +40° C., the scale being different from that in fig. 10. Table V contains the corresponding accurate numerical data. We see from the curve that there is evaporation producing a measurable vapour pressure at ordinary room temperature and even indeed at temperatures below 0° C.

The vapour pressures of some other liquids are collected in Table VI (p. 291). The lowest row of figures gives the boiling-points at the normal atmospheric pressure of 760 mm. The determination of these values can be carried out in many cases with the apparatus shown in fig. 9.

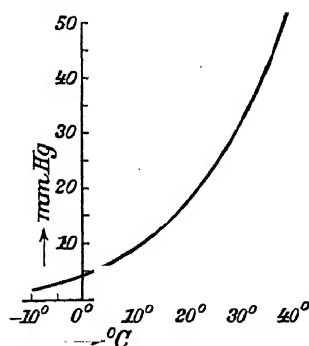


Fig. 11.—Vapour-pressure Curve for Water at Low Temperatures

5. Determination of Atmospheric Pressure from the Boiling-point.—The interpolation formula

$$t = 100 + 0.0375(b - 760)$$

has already been mentioned on p. 5. It expresses the boiling-point $t^\circ \text{C.}$ of water as a function of the barometric height b mm. of mercury within the range $715 \leq b \leq 775$. Given a reliable thermometer at least accurate enough to read correctly to 0.01°C. , the equation may be used to calculate the barometric height from the observed boiling-point $t^\circ \text{C.}$ It has been found possible to reduce the limits of error in the determination of barometric pressure by this method to ± 0.02 mm.

The value of the gravitational acceleration g varies slightly at different places on the earth. It may be determined in the following way. The atmospheric pressure indicated by the barometric height b is $0.1 b s g$ dynes/cm.², where s is the density of mercury. Hence the same atmospheric pressure will correspond to different barometric heights b_1 and b_2 at two different places where the gravitational accelerations are respectively g_1 and g_2 . These quantities will be connected by the equation $b_1 g_1 = b_2 g_2$. If now the dependence of the boiling-point upon the barometric height b_1 be known from formulæ or tables for one definite place where the gravitational acceleration is known to be g_1 , then it is possible from a determination of the boiling-point at a second place to find the barometric height which would correspond to the actual atmospheric pressure if the gravitational acceleration were g_1 . The actual barometric height at the time and place of the boiling-point determination being b_2 , the atmospheric pressure in dynes/cm.² is given by $0.1 b_1 s g_1 = 0.1 b_2 s g_2$. From this we obtain the unknown gravitational acceleration, viz. $g_2 = b_1 g_1 / b_2$. In this way by comparison of the actual barometric height with that calculated from the boiling-point it has been possible to determine the gravitational acceleration at many different places on the earth's surface—especially on the sea, where pendulum observations could not be carried out on account of the motion of the ship. The results have given very clear and unexpected information about the distribution of gravitational force on the earth's surface (HECKER, 1910).

The method of boiling-point determination can also be used with advantage to obtain barometric heights on mountains, since the necessary apparatus is more easily portable than the very fragile mercury barometer. Such an easily portable apparatus for boiling-point determinations is called a *hypsometer*.* From the barometric height it is then possible to calculate the height of the mountain by means of the altitude formula (Vol. I, p. 319).

6. Vapour Pressure of Solids.—Solids also show vapour pressures which vary with temperature in a similar manner to those of liquids. If the vapour pressure of a solid reaches atmospheric pressure at a temperature below the melting-point, the substance sublimes (*sublimation-point*). At the melting-point the vapour pressures of the solid and liquid are equal, since at this temperature both can exist together in equilibrium. (If the vapour pressures were not equal, the form with the greater vapour pressure would necessarily pass over gradually into the form with lesser vapour pressure.)

The vapour-pressure curves for water and ice are shown diagrammatically in fig. 12.

Water, ice, and water vapour can exist together in equilibrium under a

* Gr., *hypso*s, height. The method and name are due to REGNAULT.

pressure of 4.6 mm. at a temperature slightly above 0°C . (on account of the alteration of melting-point by change of pressure). This point is called the **triple point**. In the various sections of the diagram are inscribed the stable phases under the corresponding conditions of temperature and pressure. In the figure P = triple point and $C.P.$ = critical point (p. 89). The dotted curve is the melting-point curve for normal substances, i.e. substances which expand on melting.

7. Boiling-points of Solutions.—Solutions boil at higher temperatures than the pure solvent, the elevation of the boiling-point being proportional to the concentration of the dissolved substance, provided that this is not too great. The **specific elevation of the boiling-point** is that produced by 1 gm. of the dissolved substance in 100 gm. of

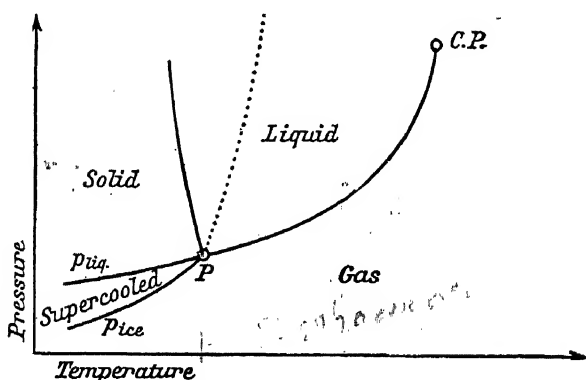


Fig. 12.—Phase Diagram for Water (not to scale)

solvent. The product of the specific elevation θ and the molecular weight μ of the dissolved substance is a constant C' of the solvent (RAOULT), i.e.

$$\mu\theta = C'.$$

The value of C' for ether is 21, for alcohol 11.6, for benzene 27, and for water 5.2.

The elevation of the boiling-point of a given solvent depends only upon the number of gramme-molecules of solute per unit of volume, being independent of the nature of the solute.

Hence the elevation of the boiling-point is used, like the depression of the freezing-point, for the determination of the molecular weight of a substance. For example, 4 gm. of cane sugar dissolved in 20 gm. of water raise the boiling-point by 0.31°C . The specific elevation is therefore $\theta = (0.31 \cdot 20)/(4 \cdot 100) = 0.0155^{\circ}\text{C}$. Hence the molecular weight is

$$\mu = C'/\theta = 5.2/0.0155 = 335 \text{ (cf. p. 63).}$$

(Ebullioscopic * method of molecular weight determination.)

* Fr., *ébullir*, to boil.

Many salts (*electrolytes*) show considerable deviations from RAOULT'S law both with regard to depression of the freezing-point and elevation of the boiling-point. These deviations are particularly marked when these substances are dissolved in water. They are explained, like the deviations from Van't Hoff's law (p. 63), as due to a splitting up of the salt molecules on solution into two or more (electrically charged) parts, known as ions (*electrolytic dissociation*). (See Vol. III.)

8. Distillation.—In distillation a liquid is changed into vapour by addition of heat, and the vapour is then brought once more into the liquid state by cooling.

Since the percentage composition of the vapour from a mixture is in general different from that of the liquid, distillation may be used with advantage to separate two liquids of different boiling-points

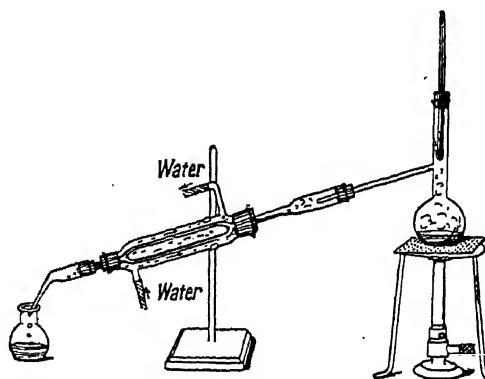


Fig. 13.—Distillation Apparatus: Distilling Flask, Liebig Condenser and Receiver

or to separate a liquid from a solid dissolved in it. Ordinary spring water or tap water contains a number of salts in solution. When it is boiled in a vessel, pure water passes off as steam and can be condensed by cooling with cold water and collected in a separate vessel.

Fig. 13 shows the kind of distillation apparatus usually employed in the laboratory. The liquid is brought to the boil in the distilling flask on the right of the figure. The temperature of the vapour can be read off on the thermometer inserted as shown. Then the hot vapour is cooled by means of cold water in the Liebig condenser, near the lower end of which it becomes liquid. The condensed product (distillate) is collected in the receiver. The direction of flow of the cooling water is opposite to that of the vapour, a method by which the cooling effect of the water is most efficiently utilized and the lowest possible final temperature of the vapour attained (*counter-current principle*).

If the distilling flask contains a mixture of two liquids with different boiling-points, e.g. alcohol and water, practically only alcohol passes over when the boiling-point of alcohol is reached. The temperature rises slowly, however, and water begins to pass over along with the alcohol. The higher the temperature, the greater the proportion of water distilling. Finally, when the boiling-point of water is reached, practically pure water passes over. The distillates for different temperature ranges are collected separately. In this way a number of different

liquid mixtures (*fractions*) is obtained, those collected at the lowest temperatures being richest in alcohol. By repeating this partial separation of alcohol from water several times for each fraction, an almost complete separation of the two substances is eventually attained (*fractional distillation*).

In many cases a complete separation of two substances by means of distillation is not possible, because of the formation of mixtures of definite percentage composition which behave like pure substances in having constant boiling points.

4. The Behaviour of Vapours

1. **Evaporation in Space filled with Gas.**—From the fact that the water in an open vessel gradually disappears we conclude that water (and also other liquids) must vaporize at room temperature in a space already filled with gas. The water evaporates, i.e. passes over into vapour, which mixes with the air. In this case the formation of vapour takes place only at the *free surface*. In *boiling*, however, it takes place for the most part in the *interior* of the liquid, namely at those points where the supply of heat first causes the vapour pressure to become equal to the pressure to which the liquid is subjected. Thus normally boiling begins at the bottom of a heated vessel. The vapour pressure in the air-free space above a liquid has already been discussed on p. 77.

The vapour from a liquid also produces a pressure in a space filled with gas. Through the doubly bored stopper of a glass bottle (fig. 14) pass one glass tube with a tap and another which is connected by means of rubber tubing with a mercury manometer. A small quantity of ethyl ether, contained in a small thin-walled glass bulb, is introduced into the bottle, the tap is closed and the bulb broken by shaking the bottle. The ether escapes out of the bulb and evaporates. The corresponding vapour pressure causes the manometer to rise, at first rapidly and then more and more slowly. After a time a constant final state is reached, in which the excess pressure as read off on the manometer is equal to the vapour pressure of the ether. It is found that this vapour pressure is exactly equal to that which would have been exerted (Table VI, p. 291) if the vapour had been formed in an air-free space.

The pressure of the air merely retards the vaporization; the partial pressure of the vapour after equilibrium has been attained is independent of the presence of other gases or vapours. (Dalton's law, 1807.)

2. **Unsaturated Vapours.**—In the experiment shown in fig. 9, p. 76, the first drops of liquid introduced into the air-free space above the mercury evaporate completely. When enough liquid has been introduced, however, a liquid layer is formed on top of the mercury. The space has then taken up all the vapour which it is able to take up



Fig. 14.—Addition of Partial Pressures

at the temperature of the experiment, and is said to be *saturated with vapour*. The vapour is also referred to as **saturated vapour**. On the other hand, when the amount of liquid introduced is so small that it has evaporated completely, and when subsequent liquid additions will also evaporate, the vapour is said to be **unsaturated**. In this case it behaves similarly to a gas, obeying Boyle's law approximately when the levelling vessel is raised or lowered. But from the moment when the raising of the levelling vessel causes the vapour to begin to condense, the pressure of the vapour (which is now saturated) remains constant. Further raising of the levelling vessel causes more vapour to condense. Lowering causes the condensed liquid to evaporate until it has all become vapour; then further lowering causes the vapour to become unsaturated.

When a vessel full of saturated vapour is heated, it becomes unsaturated; for the higher the temperature, the more vapour the given space can take up. Hence unsaturated vapours are also called **superheated vapours**. The farther the temperature of a superheated vapour is from the condensation point, the more nearly will the vapour obey Boyle's law (p. 12 and Vol. I). Hence the volume and density of a vapour at any desired temperature can be calculated by means of Boyle's and Gay-Lussac's laws from the corresponding values determined at a known pressure and a known temperature lying far above the boiling-point.

3. Vapour Density.—

The vapour density of a gas or an unsaturated vapour is that mass whose volume at 0° C. and 760 mm. pressure, as calculated by the Boyle-Gay-Lussac law, would be 1 cm^3 .

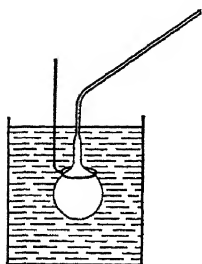


Fig. 15.—Dumas' Method of Vapour Density Determination.

By dividing the density by the mass of an equal volume of air or of hydrogen, we obtain the *vapour density relative to air or relative to hydrogen* respectively. In chemistry the vapour density is often defined as the density relative to hydrogen as unity.

DUMAS' * method of determining vapour density is as follows. A few cubic centimetres of the liquid (e.g. ether or benzene) whose vapour density is to be determined is introduced into a thin-walled glass bulb (fig. 15) with a finely drawn out point. The weight W_1 of the bulb has been previously determined. The bulb is heated in a bath up to a temperature at which all the liquid evaporates. The vapours developed drive all the air out of the bulb. When no more liquid remains unevaporated, the fine point of the bulb is sealed off, the temperature t of the bath and the barometric height b being noted simultaneously. The bulb is then removed from the bath and its weight W_2 determined. The point is then broken off under water, which enters and fills the bulb. Let the weight of the bulb full of water be W_3 . Then $(W_3 - W_1)$ gm. is the weight of the water required to fill the bulb, i.e. is equal to the volume

* JEAN BAPTISTE DUMAS (1800-84), famous chemist at the Sorbonne in Paris.

V in cm^3 of the vapour when the bulb was sealed off. The volume reduced to 0°C . and 760 mm. pressure is therefore

$$V_0 = \frac{W_3 - W_1}{1 + \alpha t} \cdot \frac{b}{760}.$$

The weight of the bulb filled with air is W_1 , the weight of the air contained in it is $(W_3 - W_1) \cdot 0.001293 \text{ gm.}$, therefore the weight of the bulb alone (as weighed in air) is

$$W_1 - (W_3 - W_1) \cdot 0.001293 \text{ gm.}$$

Hence the weight of vapour filling the bulb is

$$W = W_2 - [W_1 - (W_3 - W_1) \cdot 0.001293] \text{ gm.}$$

From this we obtain the vapour density $d = W/V_0$. The vapour density relative to air may be found by division by 0.001293.

VICTOR MEYER'S* apparatus for the measurement of vapour density is shown in fig. 16. It consists of a long glass tube with a wider cylindrical bulb B blown on its lower end. The whole of the tube with the exception of its topmost parts is surrounded by a wider cylindrical jacket, in which a liquid F is boiled by means of a flame underneath it. A few metal shavings are introduced into this outer jacket to prevent superheating. The vapour keeps the whole inner tube at the boiling-point of F. The upper end of the inner tube is provided with two side tubes. Of these R is a narrow tube whose end dips in a pneumatic trough, while S is closed by means of a piece of rubber tubing through which a glass rod is pushed until it touches the wall of the vertical tube.

The substance whose vapour density is to be determined is contained in a small bottle K, which is introduced through the upper end of the vertical tube. The glass rod pushed through S prevents the bottle from falling down to B. The upper end of the vertical tube is then closed with a stopper.

The whole apparatus is heated up until no more air bubbles escape from the side tube R. The glass rod is then drawn out a little so that the small bottle K falls into the bulb B. The liquid contained in it evaporates at once and drives out a part of the air from the inner tube. The air thus displaced is collected in a measuring jar M inverted over the end of the tube R. The volume of the air collected is equal to the volume of the vapour produced by the evaporation of the substance from the bottle. Since the volume of the air is measured after it has cooled down to room temperature in passing out of the heated tube, it is not necessary to know the temperature at which the evaporation of the substance took place. For the definition of vapour density was based upon the assumption that the vapour behaves like a perfect gas, i.e. that the volume of the vapour decreases with fall of temperature to the same extent as that of air. Room temperature and the pressure under which the air is collected must be noted. All the quantities required for the calculation of the vapour density are then known.

On account of its simplicity the Victor Meyer method of vapour density determination is much used by chemists.

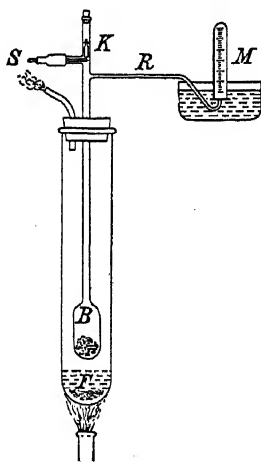


Fig. 16. — Victor Meyer's Method of Vapour Density Determination.

* VICTOR MEYER (1848-97), Professor of Chemistry at Heidelberg from 1889 as successor to BUNSEN.

4. Vapour Density and Molecular Weight.—According to Avogadro's law (p. 16) equal volumes of two different gases under the same conditions contain equal numbers of molecules. Hence the weights of the two equal volumes are in the ratio of the respective molecular weights.

Molecular weights are in the same ratio as vapour densities.

Hence one of the methods of determining molecular weight is based on the measurement of vapour density. Measurements of this kind are therefore important in chemistry.

Example.—It is known from chemical analytical methods that the elements carbon and hydrogen are contained in benzene, in the ratio 12:1 by weight. Hence from the known atomic weights ($C = 12$ and $H = 1$) we deduce that the chemical formula for benzene is C_nH_n , where n is an integer. A determination of the vapour density of benzene relative to hydrogen gives the value 39. Now the molecular weight of hydrogen is 2; hence the molecular weight of benzene must be $2 \cdot 39 = 78$. From this it follows that the formula of benzene is C_6H_6 , for only with the value $n = 6$ can the molecular weight be 78.

For other methods of molecular weight determination see pp. 70 and 79.

An interesting method of molecular weight determination from the surface tension is that of Eötvös (1886). Let V be the volume of a gramme-molecule of the liquid, α the surface tension, and T the absolute temperature. Then the energy required to produce the surface S of one gramme-molecule is αS , and therefore a numerical multiple of $\alpha V^{2/3}$. According to Eötvös the equation

$$\alpha V^{2/3} = 0.227(T_0 - T_1)$$

is fulfilled, where T_0 is the temperature at which $\alpha = 0$, i.e. the temperature at which gas and liquid are identical. This is approximately the critical temperature (p. 89). Since $V = \mu/s$, where μ is the molecular weight and s the density, it is possible to calculate μ from the observed surface tension, temperature and density.

5. Humidity

According to Dalton's law (p. 81) a space filled with a gas can go on taking up vapour from a liquid until the partial pressure of the vapour becomes equal to the vapour pressure which the saturated vapour would exert if it alone were present in the space. From this it follows that the presence of air above the surface of water merely has a *retarding* effect on the vaporization, the same saturation state being eventually reached in presence and absence of air, provided that sufficient time is allowed.

If the atmospheric air were always at the same temperature and always at rest, this saturation state would long since have been reached and would remain undisturbed. Actually, however, there are always air currents and changes of air temperature. When the temperature of the air falls so much that the actual amount of water vapour present exceeds the saturation amount, the excess is deposited as mist and

water drops. When the temperature rises again the air is no longer saturated. A considerable time elapses before the saturation state is once more attained. It follows, therefore, that the atmosphere is not in general saturated with water vapour.

Since the quantity and pressure of a saturated vapour in an air-free space increases with rise of temperature, the quantity of vapour required to saturate a space filled with air also increases in the same way. When the saturation state is reached, i.e. when the space filled with air has taken up the greatest possible amount of water vapour, the corresponding partial pressure of this vapour is called the **saturation pressure**. It is equal to the vapour pressure at the same temperature (see figs. 10 and 11, p. 76). The difference between the saturation pressure and the actual partial pressure may be called the **saturation deficiency**.

The water-vapour content of the air is called the **humidity**. It is expressed in grammes of water vapour per 1 m^3 of air. This is the **absolute humidity** and may be denoted by f . The ratio of the absolute humidity to the maximum possible content of water vapour in the saturation state at the same temperature is called the **relative humidity**. It is usually expressed as a percentage.

Table V contains the saturation pressures p and the corresponding masses of vapour per 1 m^3 for temperatures between -10°C . and $+29^\circ \text{C}$. We see from the table that 1 m^3 of air at 20°C . can only take up 17.3 gm . of water, and that the partial vapour pressure of the water vapour is then 17.5 mm . This is therefore the saturation pressure at 20°C . If now the vapour pressure of the water vapour actually present has been found to be 12.8 mm ., we see from the table (for 15°C .) that this corresponds to a content of 12.8 gm . per m^3 . (The identity of the numerical values is fortuitous.) The absolute humidity is therefore $12.8 \text{ gm}/\text{m}^3$. The difference $17.5 - 12.8 = 4.7 \text{ mm}$. is the saturation deficiency, and the quotient $12.8/17.5 = 0.74 = 74 \text{ per cent}$ is the relative humidity. If f_0 is the saturation humidity, p_0 the saturation pressure at the temperature considered, f the actual absolute humidity and p the actual partial vapour pressure, then f/f_0 is the relative humidity. At ordinary temperatures it is also approximately equal to p/p_0 .

When the air becomes cooler, the absolute humidity does not change at first; but the saturation pressure becomes smaller and hence the relative humidity increases. In the example given above the absolute humidity becomes equal to the saturation humidity when the temperature has fallen to 15°C . The saturation deficit is then zero and the relative humidity 100 per cent.

If the temperature falls still farther, a part of the water vapour condenses to mist or water drops, which form in particular upon dust particles (p. 67) (*condensation nuclei*) or other solid bodies.

The temperature at which the condensation of water vapour begins is called the **dew-point**.

The dew-point is therefore the temperature at which the actual vapour pressure would be the saturation pressure. In the example given above the dew-point is 15°C . If we know the dew-point, we can find the corresponding satura-

tion pressure and humidity from Table V; these are then respectively equal to the actual partial water-vapour pressure and absolute humidity of the atmosphere.

Measurement of Humidity. Hygrometers.*—The theoretically simplest measurement of humidity consists in passing a certain volume of air, say 1 m^3 , through a tube filled with a very hygroscopic substance (calcium chloride, concentrated sulphuric acid or phosphorus pentoxide), and weighing the tube before and after (absorption or chemical hygrometer). This kind of determination is very inconvenient to carry out, but it is the standard method for fundamental scientific measurements and the construction of tables.

Another method equally simple in theory is that involving the direct determination of the partial pressure of the water vapour present. This is done by measuring the pressure exerted by a certain quantity of atmospheric air in a closed vessel and then absorbing the water vapour completely by means of hygroscopic substances and measuring the pressure again. This method is also inconvenient to carry out.

Dew-point Hygrometers.—The basic principle of dew-point hygrometers for the determination of the dew-point is that a part of the instrument, whose temperature can be measured easily, is cooled down until it becomes covered with a deposit of moisture, i.e. until the dew-point

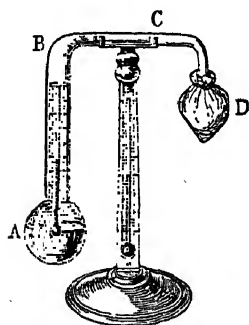


Fig. 17.—Daniell's Dew-point Hygrometer

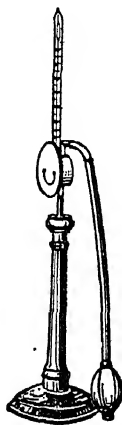


Fig. 18.—Lambrecht Dew-point Hygrometer

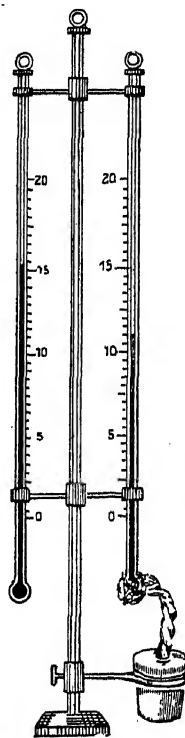


Fig. 19.—August's Psychrometer or Wet and Dry Bulb Hygrometer

is reached. The oldest (and least dependable) dew-point hygrometer is that of DANIELL† (fig. 17). A U-shaped glass tube BC with bulbs at each end is evacuated, filled with ether and ether vapour and sealed off. The bulb D on the shorter limb is covered with light cloth; the bulb A on the longer limb is gilded on the outside and fitted with a thermometer inside. Liquid ether is poured gently on to the cloth surrounding the bulb D. It evaporates and thus cools down the ether vapour inside the tube and causes it to condense. There is a decrease of pressure inside D, as a result

* Gr., *hygrós*, wet.

† JOHN FREDERICK DANIELL (1790–1845), English physicist, Professor of Chemistry in King's College, London, and inventor of Daniell's cell, described his hygrometer in 1820.

of which the ether inside the gilded bulb A evaporates. Thus the bulb A is also cooled. Its temperature is read off at the moment when it becomes dimmed with a film of moisture, and then again when the deposit of moisture disappears. The mean of the two readings is the dew-point. The corresponding absolute humidity is read off from Table V, and the relative humidity can then be calculated.

A more recent form is the **Lambrecht dew-point hygrometer** (fig. 18). This consists of a thin-walled, highly-polished metal box into which pass a thermometer and a tube. The box is filled with ethyl ether. Air is blown into the ether by means of a rubber bulb, the ether evaporates quickly, the box is cooled down. It becomes coated with a film of moisture at the dew-point, which can be read off on the thermometer. The metal box is surrounded by a flange of the same metal, so that the difference between the dimmed box and the bright flange may be easily observed.

August's Psychrometer* (1825) or **Wet- and Dry-bulb Hygrometer**.—This apparatus (fig. 19) consists of two exactly similar thermometers. The bulb of one of these is wrapped round with light cloth. This is moistened with water, which condenses and withdraws heat from the thermometer, thus cooling the bulb. The farther the air is from the saturation state, the faster the evaporation of the water and the greater the cooling. Hence the difference of the readings of the two thermometers gives a measure of the saturation deficit and hence also of the absolute humidity. If t is the temperature of the dry-bulb thermometer, t' that of the wet-bulb thermometer, f' the saturation humidity for the temperature t' and b the barometric height, then the required absolute humidity is given by the equation

$$F = f' - Ab(t - t').$$

Here A is a constant. If t' is above 0°C. , A may be put equal to 0.0008; when t' is below 0°C. , $A = 0.00068$. In practical use the values of F are obtained from special *psychrometric tables*.

If the air is still the layer immediately surrounding the wet bulb may easily become saturated with water vapour and thus make the observed humidity too great. The thermometer or the air must therefore be set in motion before the reading is taken. This can be done most simply by arranging both thermometers in a common frame and whirling the whole about 100 times in a circle at the end of a strong string (**centrifugal psychrometer**), or by enclosing both thermometers in a case through which air is constantly sucked by means of a small clockwork fan (**aspiration psychrometer** of ASSMANN.†)

Hair Hygrometer.—In this hygrometer (fig. 20) use is made of the fact that organic materials will take up moisture from humid air and thereby change in size. A stretched human hair freed from grease becomes longer in moist air. If such a hair be fixed at one end and wound round the axis of a pointer,

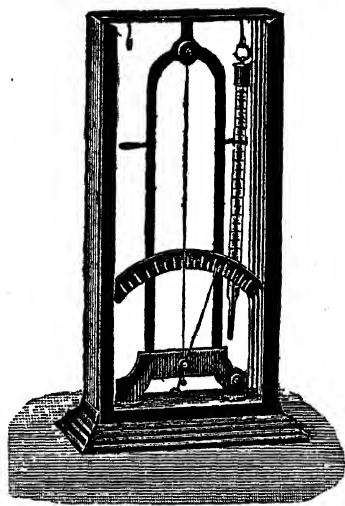


Fig. 20.—Hair Hygrometer after Koppe

* Gr., *psychrós*, cold.

† RICHARDT ASSMANN, died 1918, Director of the Aeronautical Observatory at Lindenberg, 1915–18 Professor at Giessen.

the latter will be moved when the length of the hair varies.* The relative humidity can thus be read off directly. The scale must be calibrated empirically. The reading is convenient; but the results are not completely dependable. Since hair hygrometers are very simple and have the remarkable property of giving the relative humidity practically independently of the temperature, they are also much employed in conjunction with registering apparatus in the meteorological investigation of the upper atmosphere (balloon and kite experiments).

The same principle is embodied in the weather indicators made in the form of a little house, at the top of which is fixed a catgut string carrying a cross beam at its lower end with two small figures upon it. When the relative humidity is great, the catgut string turns in one direction; when the relative humidity is small, it turns in the other.

6. The Liquefaction of Gases

When the levelling vessel of fig. 9, p. 76, is raised at constant temperature, the difference of level in the two tubes, i.e. the vapour pressure, remains constant from the moment at which the first traces of condensed liquid are visible above the mercury. If now the temperature of the jacket be raised, the liquid vaporizes once more; but the vapour can be liquefied again by higher pressure. The liquefaction of a vapour begins as soon as the external pressure reaches the saturation vapour pressure at the temperature of the experiment.

There are two general methods of liquefying a gas, namely, lowering of temperature and increase of pressure. Many substances (e.g. carbon dioxide, sulphur dioxide, ammonia, &c.) which are gaseous at ordinary temperature and pressure can be liquefied by either method. Other gases, in particular hydrogen and the constituents of the air, cannot be liquefied at ordinary temperature even by a pressure of 3000 atmospheres.

ANDREWS † explained this in 1869 by subjecting carbon dioxide to increasing pressures at different constant temperatures and investigating carefully the attendant phenomena.

At 13.1°C . the volume of the carbon dioxide under 47.5 atm. pressure was $13.13 \cdot 10^{-3}$ of the original volume. Further compression caused further decrease of volume; at 48.8 atm. pressure the volume was $12.4 \cdot 10^{-3}$ of the original. Liquefaction then began and there was a continuous decrease of volume to $2.1 \cdot 10^{-3}$ of the original, the pressure remaining constant at first and then finally rising to 50 atm. All the carbon dioxide was now liquid. A further increase of pressure to 100 atm. only decreased the volume to $1.96 \cdot 10^{-3}$ of the original.

In fig. 21 the lowest dotted curve is the corresponding isotherm (p. 15) of carbon dioxide for 13.1°C . The isotherm for 21.5°C ., as observed by ANDREWS, is also shown. Both isotherms have the common property of running almost

* The hair hygrometer was first described in 1783 by HORACE DE SAUSSURE (1740-99).

† THOMAS ANDREWS (1813-85), Irish chemist and physicist, Vice President and Professor of Chemistry at Queen's College, Belfast, from 1845 to 1879. Awarded the Royal Society medal in 1844 for work upon the heat developed in chemical reactions. He is famous chiefly, however, on account of his work in connexion with the liquefaction of gases.

horizontally for a considerable volume range, namely in the region B in which liquefaction takes place, and where the carbon dioxide exists in both gaseous and liquid states side by side.

The horizontal part of the isotherm for 21.5°C. is shorter than that of the isotherm for 13.1°C. As the temperature rises the horizontal part becomes shorter and shorter. The isotherm for 31.1°C. no longer has any horizontal section, i.e. there is a continuous decrease of volume with increase of pressure. In this case no liquefaction of the carbon dioxide occurs, no matter how much the pressure is

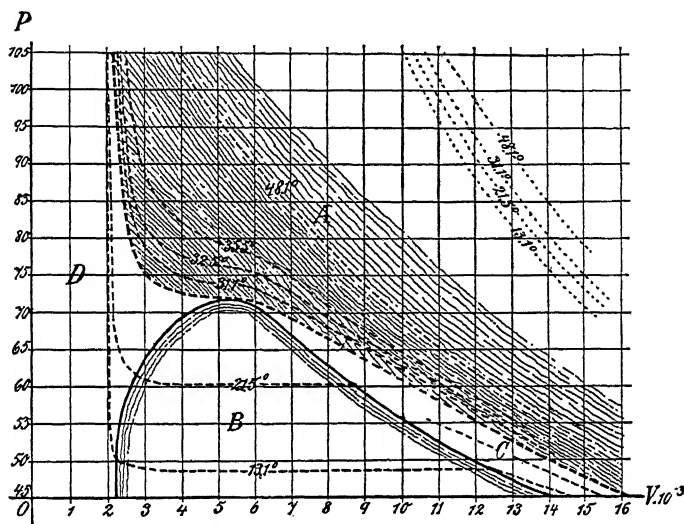


Fig. 21.—Isotherms of Carbon Dioxide

A + C = Region of Gas; D = Region of Liquid; B = Region of Co-existence of Liquid and Gas. P, in atmospheres. Critical Point 30.9°C. Dotted curves (top right) are isotherms of a perfect gas.

increased. There is only a point of inflection in the isotherm indicating the point at which condensation would take place at lower temperatures. With further increase of temperature the inflection also disappears more and more completely. In the isotherm for 48.1°C. there is no trace of it.

For purposes of comparison some isotherms of a perfect gas for the same temperatures are shown to the right of the diagram. We see that carbon dioxide is very far from obeying the ideal gas laws under these conditions. This is the case in general for all gases in the neighbourhood of their condensation points or under high pressures (see next section).

The temperature at which the horizontal part of the curves just vanishes is called the **critical temperature**, and the point at which the isotherm for this temperature touches the curve bounding the region B of coexistence of liquid and gas is called the **critical point**. This is the highest point of the region B.

The whole phase diagram of carbon dioxide is divided into two essentially different regions by the isotherm for the critical temperature. Above the critical temperature in the region A no liquid state is possible for carbon dioxide even under the greatest pressures. Below the isotherm for the critical temperature every isotherm passes from a region C in which the carbon dioxide is completely gaseous, through a region B in which it is partly gaseous and partly liquid, and finally into a region D in which it is completely liquid.

The most important result of ANDREWS' investigation is the following:

For every vapour or gas there exists a critical temperature above which liquefaction by pressure is impossible.

Thus the region of existence of the liquid state vanishes altogether above the critical temperature (cf. fig. 12, p. 79).

Below it, at a given temperature the substance is gaseous at low pressures, then at a higher, practically constant pressure it passes through a region of coexistent gaseous and liquid states, becoming completely liquid when the pressure is still further increased. The critical temperatures of some substances are given in Table VII (p. 292).

The phenomena connected with critical temperature can be conveniently observed in a sealed glass tube partly filled with liquid carbon dioxide. At ordinary temperature the division between the liquid and gaseous carbon dioxide is sharp. When the tube is warmed in a water bath, however, the division vanishes completely at 31°C . with the appearance of a peculiar opalescence (see p. 141); for at and above this temperature carbon dioxide can no longer exist in the liquid state.

The vapour pressure at the critical temperature is called the **critical pressure** (Table VII).

When the existence of a critical temperature and the nature of the phenomena connected with it had been recognized, it also became clear why in many cases the previous attempts to liquefy gases by pressure had failed: the attempts had been made at temperatures above the critical temperatures. After ANDREWS' investigations CAILLETET in Paris and PICTET in Geneva (1877) first succeeded in liquefying the constituents of the air by using low temperatures. Later followed the liquefaction of hydrogen by OLSZEWSKI (1895) and J. DEWAR (1898), who was the first to liquefy large quantities. Finally in 1908 KAMERLINGH-ONNES also succeeded in liquefying helium at Leiden at a temperature of -268.71°C . Nowadays, since LINDE of Munich has made possible (1895) the production of low temperatures by the method described in § 6, p. 109, the liquefaction of gases no longer presents any difficulties.

7. Van der Waals' Equation of State

As is seen from fig. 21, the volume at a given pressure is much smaller for carbon dioxide than for a perfect gas (dotted curve at the top of the figure to the right). Thus a given pressure is able to produce a greater compression in the case of carbon dioxide than in the case of a perfect gas. It is plausible to assume that the reason for this may lie partly in the molecular forces of cohesion, which were regarded as negligibly small in the derivation of the laws for perfect gases. A further assumption made in the derivation of the ideal laws was that the space actually occupied by the molecules themselves is negligibly small in comparison with the volume of the space in which the gas is confined. The error introduced by this assumption must become noticeable under high pressures, when the gas is compressed to a small fraction of its volume at atmospheric pressure. For the purposes of the present treatment we may regard the molecules as rigid elastic spheres. Thus even when they are packed together as closely as possible, the gas

will still occupy a certain volume b . In addition the outward pressure of the gas upon the walls of the containing vessel, which has been calculated exclusively from the rectilinear velocities of the molecules, will be decreased by the intermolecular forces of attraction. These are the same forces with which we have already become acquainted as forces of cohesion in the case of denser molecular disposition. The effect of such forces of attraction vanishes on the whole for molecules in the interior of the space in which the gas is confined. It becomes apparent, however, at the boundaries, as an inward attraction upon the surface molecules. Hence the total effect is the same as if the external pressure p upon the gas were increased by an amount α . Now on the one hand α is proportional to the number of attracted molecules per unit area of the boundary surface. Hence it must be proportional to the total number of molecules per unit volume, and therefore inversely proportional to the volume V of the gas. On the other hand, α is also proportional to the number of attracting molecules, i.e. proportional to the number of molecules per unit volume and again (for a second reason) inversely proportional to the volume V . We may therefore write $\alpha = a/V^2$, where a is a constant. Since the gas molecules are of finite size, the total volume V at their disposal must be diminished by the amount b in order to obtain the free volume to which the Boyle-Gay-Lussac law refers. As a result of these considerations VAN DER WAALS* modified the Boyle-Gay-Lussac law $pV = \nu RT$ by the addition of two terms, thus setting up the *equation of state of real gases* which is known by his name:

$$(V - b) \left(p + \frac{a}{V^2} \right) = \nu RT.$$

It has been found to hold well for many gases. It is especially important because it does not break down for the transition from the gaseous to the liquid state, and permits of the calculation of the critical temperature and *cohesion pressure* a/V^2 of liquids. The constants a and b have definite specific values for each gas. Taking 1 m. of mercury as the unit of pressure and the volume of 1 kg. of gas at 0°C . and 1 m. mercury pressure as the unit of volume, and substituting $\nu = 10^3/\mu$ in the above formula (μ = molecular weight), we obtain the following mean values of a and b :

Air:	$a = 0.0037,$	$b = 0.0026;$
Carbon Dioxide:	$a = 0.0115,$	$b = 0.003;$
Hydrogen:	$a = 0,$	$b = 0.00069.$

According to DANIEL BERTHELOT (1903) an equation of state

$$(V - b) \left(p + \frac{a}{TV^2} \right) = \nu RT$$

is in better agreement with observation at very high pressures and high temperatures. Here the *cohesion pressure* $\alpha = a/TV^2$ is inversely proportional to the absolute temperature. A corresponding equation for carbon dioxide had been previously proposed by CLAUSIUS.

* JOHANNES DIETRICH VAN DER WAALS, 1837-1923, Professor at Amsterdam from 1877 onwards, formulated his equation of state in 1873. He was NOBEL prize-winner in 1910.

CHAPTER IV

Thermodynamics

1. First Law of Thermodynamics

It has already been explained in detail above (p. 35 *et seq.*) that heat must be regarded as a form of kinetic energy, namely, the kinetic energy of the random motion of the molecules. A quantitative transformation of mechanical work into heat is possible, and the equivalence of work and heat forms the *first law of thermodynamics*. Confining ourselves to mechanical and thermal changes, the equation

$$dQ = K(dU + p dV)$$

of p. 34 states that the quantity of heat dQ developed or used up is equivalent to the change of internal energy of the system under consideration together with the external work $p dV$ performed by or upon the system. We will consider below the nature of this equivalence in certain special cases.

2. Adiabatic Changes of a Gas

1. The Relationship between the Specific Heats.—To calculate the specific heat c_p of a gas at constant pressure we transform the general equation for c (p. 34) by means of the equation of state (p. 16) for unit mass of a gas, viz.

$$pV = \nu RT,$$

where ν is the number of gramme-molecules contained in unit mass of the gas. For this purpose we differentiate the last equation with regard to T and obtain

$$p \frac{dV}{dT} + V \frac{dp}{dT} = \nu R.$$

We then substitute the value for $p dV/dT$ from this equation in the general equation for c , obtaining

$$c = K \left(\frac{dU}{dT} + \nu R - V \frac{dp}{dT} \right).$$

The pressure p of the gas being constant, we have $dp/dT = 0$ and the value of the specific heat of the gas at constant pressure becomes

$$c_p = K \left(\frac{dU}{dT} + \nu R \right) = K \frac{dU}{dT} + K \nu R.$$

Since now (p. 34)

$$c_v = K \frac{dU}{dT},$$

we have

$$c_p = c_v + K\nu R$$

or

$$c_p - c_v = K\nu R.$$

2. **Poisson's Law.**—If we assume the correctness of R. Mayer's calculation (p. 30) of the mechanical equivalent of heat from the difference of the specific heats of a gas at constant pressure and constant volume, we can deduce that a gas must become hotter by compression and cooler by expansion, provided that these changes are carried out without heat being supplied to or withdrawn from the gas. In fig. 17, p. 30, the air has a greater heat content in the state ABEF than in the state ABCD. Hence if it be brought by pressure from the former state into the latter, its temperature must rise.

This experiment is actually carried out in the case of the pneumatic tinder box. A cylindrical tube (fig. 1), generally made of glass, is closed at one end with an air-tight cap and at the other with an air-tight movable piston. At the end of the piston there is a small hollow to receive the tinder. If the piston be forced rapidly into the cylinder by the application of great pressure and then immediately withdrawn, it is observed that the tinder has ignited. The temperature of the air has been raised by the compression to the ignition point of the tinder.



Fig. 1.—
Pneumatic
Tinder
Box

When a gas in a closed space is subjected to a change of pressure, its temperature being kept *constant* by simultaneous supply or withdrawal of heat, the change is said to be **isothermal**. Boyle's law, $pV = \text{const.}$, holds for such isothermal changes, p being the pressure and V the volume of the enclosed gas.

On the other hand, when the walls of the enclosure are impervious to heat, so that no heat can either enter or leave the gas, every change of pressure is accompanied by a change of temperature. This kind of change is said to be **adiabatic**.*

According to Boyle's law the pressure of a gas is doubled when its volume is compressed to a half, say in the pneumatic tinder box by pushing in the piston. This is actually true, provided that the compression be carried out so slowly that the gas is all the time in temperature equilibrium with the surroundings. If, however, the compression to half the original volume is carried out very rapidly, i.e. adiabatically, the pressure will be more than doubled on account of the simultaneous rise of temperature.

For adiabatic changes we have Poisson's law (1882) †,

$$pV^\gamma = \text{const.},$$

in place of Boyle's law. Here p is the pressure and V the volume as before, and $\gamma = c_p/c_v$ is the ratio of the specific heats of the gas.

3. **Proof of Poisson's law.**—Fig. 2 shows three different conditions O, I,

* Gr., *a*, not; *diá*, through; *batos*, passable.

† S. D. POISSON (1781–1840), one of the greatest of French scientists, remarkable for his versatility. He made important discoveries in all branches of pure and applied mathematics.

II, of a certain mass m of gas enclosed in a cylinder fitted with an air-tight movable piston. In the first condition O the gas has the volume V_0 at a pressure p_0 and absolute temperature T_0 . A certain quantity Q of heat is added to the gas, the piston being held at the same position. Thus in the condition I we have the same volume $V_1 = V_0$. The corresponding rise in temperature from T_0 to T_1 is accompanied by an increase of pressure from p_0 to p_1 . By the Boyle-Gay-Lussac law we have

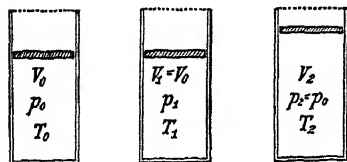


Fig. 2.

$$\frac{p_1}{T_1} = \frac{p_0}{T_0} \quad \text{or} \quad p_1 = p_0 \frac{T_1}{T_0}.$$

The condition II is reached from the condition O by the addition of the same quantity Q of heat, the piston now being free to move and the pressure remaining constant, $p_2 = p_0$.

The volume V_0 increases to V_2 , while the temperature rises simultaneously from T_0 to T_2 . By the Boyle-Gay-Lussac law

$$V_2 = V_0 \frac{T_2}{T_0}.$$

Making use of the specific heat c_v of the gas at constant volume, the rise of temperature during the transition from condition O to the condition I is given by the equation

$$Q = mc_v(T_1 - T_0),$$

whence
$$T_1 - T_0 = \frac{Q}{mc_v}, \quad \text{i.e.} \quad T_1 = T_0 + \frac{Q}{mc_v}$$

In the same way the rise of temperature ($T_2 - T_0$) can be calculated in terms of the specific heat c_p of the gas at constant pressure, viz.:

$$Q = mc_p(T_2 - T_0),$$

whence
$$T_2 - T_0 = \frac{Q}{mc_p}, \quad \text{i.e.} \quad T_2 = T_0 + \frac{Q}{mc_p}$$

The temperatures, volumes and pressures in the three conditions O, I and II are given below in tabular form:

Condition	O	I	II
Temperature ..	T_0	$T_1 = T_0 + \frac{Q}{mc_v}$	$T_2 = T_0 + \frac{Q}{mc_p}$
Volume	V_0	$V_1 = V_0$	$V_2 = V_0 \frac{T_2}{T_0}$
Pressure	p_0	$p_1 = p_0 \frac{T_1}{T_0}$	$p_2 = p_0$

If the gas be brought from the condition I to the condition II by raising the piston without supply or withdrawal of heat, the change is an adiabatic one. The following changes take place:

1. The volume is increased by the amount

$$V_2 - V_1 = V_1 \frac{T_2 - T_0}{T_1}$$

2. The pressure is diminished by the amount

$$p_1 - p_2 = p_2 \frac{T_1 - T_0}{T_0}$$

3. The temperature is lowered by the amount

$$T_1 - T_2 = \frac{Q}{m} \left(\frac{1}{c_v} - \frac{1}{c_p} \right).$$

Dividing 2 by 1 we obtain

$$\frac{p_1 - p_2}{V_1 - V_2} = - \frac{p_2}{V_1} \frac{(T_1 - T_0)}{(T_2 - T_0)}.$$

Now from the values

$$T_1 - T_0 = \frac{Q}{mc_v} \quad \text{and} \quad T_2 - T_0 = \frac{Q}{mc_p}$$

(see the above table) we have

$$\frac{T_1 - T_0}{T_2 - T_0} = \frac{c_p}{c_v} = \gamma.$$

Substituting this in the equation just obtained, it follows that

$$\frac{p_1 - p_2}{V_1 - V_2} = - \frac{p_2}{V_1} \gamma$$

or

$$\frac{p_1 - p_2}{p_2} = - \frac{V_1 - V_2}{V_1} \gamma.$$

Since $p_2 = p_0$ and $V_1 = V_0$, it follows further that

$$\frac{p_1 - p_0}{p_0} = - \frac{V_0 - V_2}{V_0} \gamma.$$

Now imagine the two conditions I and II to differ very little from one another. We may then put

$$p_1 - p_0 = \Delta p \quad \text{and} \quad V_0 - V_2 = \Delta V,$$

thus obtaining the equation

$$\frac{\Delta p}{p} = - \gamma \frac{\Delta V}{V}.$$

Proceeding to the limit when both Δp and ΔV become vanishingly small, we have

$$\frac{dp}{p} = - \gamma \frac{dV}{V}.$$

Integration gives

$$\log_e p = - \gamma \log_e V + \text{const.}$$

or

$$\log_e p + \gamma \log_e V = \text{const.}$$

Getting rid of the logarithms we have at once

$$pV^\gamma = \text{const.}$$

This is Poisson's law for adiabatic changes.

Dividing the equation of Poisson's law by the equation of state

$$\frac{pV}{T} = \nu R,$$

which holds for all gases, we obtain the new equation

$$TV^{\gamma-1} = \text{const.}$$

If the equation of state be raised to the γ th power and then divided by the equation of Poisson's law, we have

$$\frac{p^\gamma}{T^\gamma} = \text{const.}$$

Use is made of this equation for the calculation of the rise of temperature accompanying the compression of a gas or the fall of temperature accompanying expansion.

Alternative Proof.—Poisson's law can be derived directly from the first law of thermodynamics (p. 34) by putting $dQ = 0$; for the essential characteristic of adiabatic changes is that no heat is either supplied or withdrawn. In this way we at once obtain the equation

$$0 = K \left(\frac{dU}{dT} + p \frac{dV}{dT} \right).$$

In accordance with p. 34 we substitute

$$K \frac{dU}{dT} = c_v,$$

and obtain

$$c_v dT = -Kp dV.$$

Dividing this equation by the equation

$$T = \frac{pV}{\nu R},$$

which follows at once from the general equation of state for gases, we have

$$\frac{dT}{T} = -\frac{K\nu R}{c_v} \frac{dV}{V}.$$

Integration of this between the limits T_0 and T on the left-hand side and V_0 and V on the right gives

$$\int_{T_0}^T \frac{dT}{T} = -\frac{K\nu R}{c_v} \int_{V_0}^V \frac{dV}{V},$$

$$\text{i.e.} \quad \log_e T - \log_e T_0 = \frac{K\nu R}{c_v} (\log_e V_0 - \log_e V),$$

$$\text{or} \quad \log_e \left(\frac{T}{T_0} \right) = \frac{K\nu R}{c_v} \log_e \left(\frac{V_0}{V} \right).$$

Getting rid of the logarithms, we have

$$\frac{T}{T_0} = \left(\frac{V_0}{V} \right)^{\frac{K\nu R}{c_v}}.$$

Now $KvR = c_p - c_v$ (p. 93), and hence

$$\frac{KvR}{c_p} = \frac{c_p}{c_v} - 1 : \gamma - 1.$$

Substituting this in the equation just obtained, we have

$$\frac{T}{T_0} = \left(\frac{V_0}{V}\right)^{\gamma-1} \text{ or } TV^{\gamma-1} = T_0V_0^{\gamma-1} = \text{const.}$$

This is a form of Poisson's law already deduced above.

4. **Change of Temperature accompanying the Adiabatic Change of a Gas.**—
From the equation

$$\frac{p^{\gamma-1}}{T^{\gamma}} : \text{const.}$$

it follows that

$$\frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)^{1-1/\gamma}$$

and hence that

$$T_2 - T_1 = T_1 \left[\left(\frac{p_2}{p_1}\right)^{1-1/\gamma} - 1 \right].$$

Example 1.—Consider the compression of air in the pneumatic tinder box from atmospheric pressure to a pressure of 10 atmospheres. In this case $p_2/p_1 = 10$. Let the original temperature of the air be 17°C. , i.e. $T_1 = 273 + 17 = 290^\circ \text{abs.}$ Then

$$\begin{aligned} T_2 - T_1 &= 290(10^{1-1/\gamma} - 1) = 290(10^{0.286} - 1) \\ &= 290(1.93 - 1) = 290 \cdot 0.93 = 270. \end{aligned}$$

Thus the temperature of the air rises by 270°C. , i.e. to 287°C. , and the tinder is thereby ignited.

Example 2.—Let a quantity of atmospheric air ascend from the surface of the earth (where the barometric height is b_0 and the absolute temperature T_0) to the altitude h (barometric height b). It thereby cools down adiabatically by the amount

$$\Delta T = T_0 \left[\left(\frac{b}{b_0}\right)^{1-1/\gamma} - 1 \right].$$

Now according to the barometric formula for altitude (Vol. I) we have

$$h = 18400 (\log b_0 - \log b),$$

whence

$$\frac{b}{b_0} = 10^{-\frac{h}{18400}}.$$

Consequently the fall in temperature is

$$\Delta T = T_0 \left[10^{-\frac{h(1-1/\gamma)}{18400}} - 1 \right].$$

Let $h = 100 \text{ m.}$ and the air temperature t_0 at the earth's surface be 17°C. , i.e. $T_0 = 290^\circ \text{abs.}$ Then

$$\Delta T = 290(10^{-0.00155} - 1) = -1.04,$$

i.e. the temperature falls approximately 1°C.

In the above calculation we have assumed that the air is perfectly dry. For damp air the conditions are somewhat different. We will suppose that the relative humidity is about 50 per cent. In this case the temperature falls at first in strict accordance with the equation obtained above. During this phase the absolute

humidity remains constant, but the relative humidity increases until the air becomes saturated at a certain temperature. From this point onwards the fall of temperature is accompanied by a condensation of water vapour to liquid water, a process involving liberation of heat of condensation. The consequence is that the temperature now falls more slowly than would be expected according to the above formula. We see therefore that in general the fall of temperature with increase of altitude is less than that calculated above. Actual observations have shown that on the average a fall of temperature of 1°C . corresponds to 200 m. increase of altitude.

On account of the adiabatic cooling of ascending air currents and the continual exchange between the upper and lower layers, the air at great altitudes must be colder than that near the earth's surface. It follows also that when damp winds are forced upwards by mountain masses, they must give up a part of their water vapour content by condensation. This is the explanation of the heavy rainfall in all mountain districts which are subject to moist ocean winds (Norway, the Alps, the Himalayas). After passing over the mountain ridge the winds descend again and warm up once more; they then possess a very small relative humidity (e.g. the Föhn wind).

3. Determination of c_p/c_v (Clément-Desormes *)

A glass bottle G (fig. 3) of about 1 litre capacity is closed with a doubly bored stopper, through which pass two tubes, one with a wide bore tap H and the other bent into the form of a manometer M . The

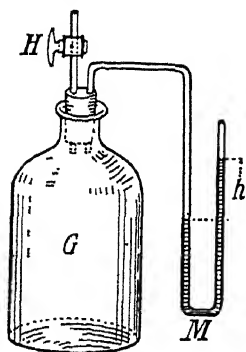


Fig. 3.—Clément and Desormes' Experiment

manometer liquid is coloured water. When a small quantity of air is blown into the bottle the air pressure inside is increased and the manometer at once indicates a corresponding difference of level h . But on account of the adiabatic nature of the compression this is not the final indication of the manometer. The final difference of level h_1 is not attained until the temperature of the air inside the bottle has become equal to that of the air outside.

The tap H is now opened for a short time just sufficient for the internal and external pressures to become equal, and then closed again. The manometer again begins to rise, reaching after a while the final constant difference of level h_2 . The explanation of this effect is that the compressed air expands adiabatically and therefore cools down when the tap is opened. After the tap has been closed again an equalization of temperature occurs, the air in the bottle warming up to the temperature of the outer air. This rise of temperature causes the increase of pressure observed on the manometer. The final pressure is, of course, smaller than the initial pressure.

The two manometer readings h_1 and h_2 are related to the specific

* This experiment was published in the year 1819 by CLÉMENT (1779–1842) and DESORMES (1777–1862) (see also Vol. I, p. 350).

heats of air at constant pressure (c_p) and constant volume (c_v) by the equation

$$\frac{c_p}{c_v} = \frac{h_1}{h_1 - h_2}.$$

Hence the Clément-Desormes experiment allows of a simple determination of the ratio $\gamma = c_p/c_v$.

Let the temperature of the air surrounding the bottle be T_1 and the atmospheric pressure p_0 . The pressure $p_1 = p_0 + h_1$ is obtained from readings of the barometer and manometer. Then $p_1 - p_0 = h_1$. We open the tap H of the Clément-Desormes apparatus (fig. 3), and the air expands adiabatically until its pressure falls to p_0 . Let it cool down to the temperature T_2 during this expansion. We immediately close the tap again and the temperature of the interior of the bottle rises to room temperature T_1 . Since the volume of the flask remains constant, the pressure rises to the new value p_2' , which by Gay-Lussac's law is given by

$$p_2' = p_0 \frac{T_1}{T_2}.$$

This pressure is read off on the manometer as a difference of level h_2 , i.e. $p_2' = p_0 + h_2$.

Hence we have
$$h_2 = p_2' - p_0 = p_0 \frac{(T_1 - T_2)}{T_2}.$$

Applying Poisson's law in the form (p. 96)

$$\frac{p\gamma-1}{T\gamma} = \text{const.}$$

to the adiabatic change, we obtain

$$\frac{p_1^{\gamma-1}}{T_1^\gamma} = \frac{p_0^{\gamma-1}}{T_2^\gamma}$$

or
$$\left(\frac{p_0 + h_1}{p_0}\right)^{\gamma-1} = \frac{T_1}{T_2} = \left(1 + \frac{T_1 - T_2}{T_2}\right)^\gamma.$$

Now let h_1/p_0 and $(T_1 - T_2)/T_2$ be small in comparison with 1. Then expanding and neglecting higher powers, we may write the equation in first approximation as follows:

$$1 + (\gamma - 1) \frac{h_1}{p_0} = 1 + \gamma \frac{T_1 - T_2}{T_2},$$

whence

$$p_0 \frac{T_1 - T_2}{T_2} = \frac{\gamma - 1}{\gamma} h_1.$$

In combination with the equation

$$h_2 = p_0 \frac{T_1 - T_2}{T_1}$$

obtained above, this gives

$$\frac{\gamma - 1}{\gamma} h_1 = h_2$$

or

$$\gamma = \frac{h_1}{h_1 - h_2}.$$

From the above calculation it follows that relatively accurate values of γ can only be obtained by the Clément-Desormes experiment provided that the compressions or rarefactions are small.

4. Isothermal and Adiabatic Curves

By plotting the volumes of a gas as abscissæ and the corresponding pressures as ordinates, we obtain a curve representing the changes of condition of the gas. As has already been shown in chapter I, at fig. 10, p. 14, the Boyle-Gay-Lussac law gives a system of rectangular hyperbolas. Each hyperbola holds for a definite temperature, and is therefore an isothermal curve. Adiabatic changes can be represented similarly by means of an adiabatic curve.

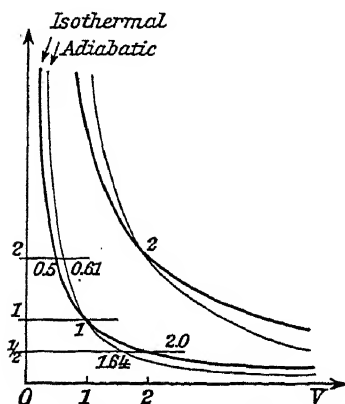


Fig. 4.—Isothermal and Adiabatic Curves

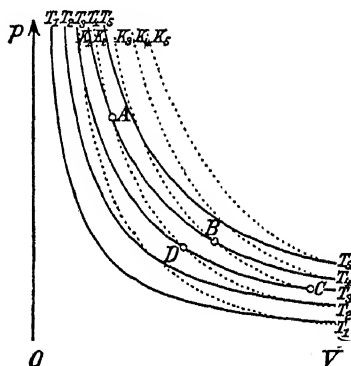


Fig. 5.—A Closed Figure ABCD made up of Arcs of Isothermal and Adiabatic Curves. (T = Isothermal, K = Adiabatic.)

In fig. 4 the two heavy lines are isothermals and the two lighter lines are adiabatics. In the case of the pair of curves lying nearer to the axes, the initial state of the gas has been taken as that represented by the point (1, 1). Whereas the isothermal curve is a rectangular hyperbola, the adiabatic lies above it at higher pressures and below it at lower pressures.

Thus if the pressure is doubled, the volume of a gas is halved when the change is isothermal (Boyle's law); but when the change is adiabatic, the volume only decreases to 0.61 of its original value in the case of air (Poisson's law). This is due to the rise of temperature accompanying adiabatic compression. If the pressure be reduced to half, the volume of a gas is doubled when the change is isothermal; but when the change is adiabatic, the volume only increases to 1.64 of its original value in the case of air. This is due to the fall of temperature accompanying adiabatic expansion.

The other pair of curves (isothermal and adiabatic) intersecting at the point (2, 2) represent the condition of the same mass of gas as before but at an absolute temperature four times as great as for the first pair of curves.

Since the adiabatic curves lie above the isothermal curves at high pressures and below them at low pressures, each adiabatic must intersect all the isothermals; the intersection with the isothermals of lower temperature will lie at lower pressures and vice versa. Fig. 5 shows five isothermal and five adiabatic curves and their points of intersection.

Particular interest attaches to the fact (which follows at once from what has been said above) that it is possible to get from any point of the (p, V) plane to any other point by means of an adiabatic and an isothermal change of the gas. Thus, for example, we can pass from the point A to the point C by going first from A to B along the isothermal curve T_4 and then from B to C along the adiabatic K_3 . Alternatively we may go first from A to D along the adiabatic K_2 and then from D to C along the isothermal T_3 .

5. Work associated with Change of State of a Gas

Consider a mass of gas of volume V enclosed in a cylinder of cross-sectional area A by means of an easily movable, weightless piston loaded with a weight P (fig. 6). The weight exerts a pressure $p = P/A$ per unit area of cross-section of the cylinder. If the length of the enclosed cylinder of gas is h , we have $V = Ah$.

Now imagine the gas to expand by a volume ΔV , thereby raising the piston a distance Δh . Then $\Delta V = A \Delta h$. Assuming that the volume change is so small that the pressure may be regarded as constant throughout, the work performed by the gas in expanding is

$$\Delta W = P \Delta h = A p \frac{\Delta V}{A} = p \Delta V.$$

In the graphical representation (fig. 7) this work corresponds to the area of a small rectangular strip. Thus the rectangle ABCD represents the work involved in the isothermal change CD of the gas. In the same way the rectangle EFGH represents the work involved in the adiabatic change GH.

In order to calculate the work performed during a greater change of condition, we must divide up the total change into elementary steps, for each of which the pressure may be regarded as constant. We can then calculate each element of work by means of the above formula, and finally obtain the total

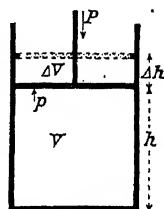


Fig. 6.—Work performed in Compressing a Gas

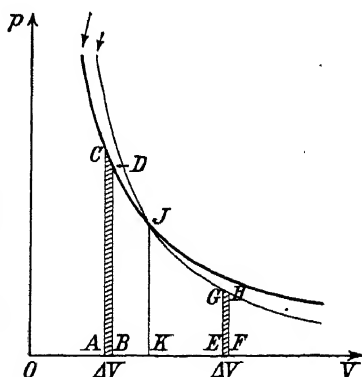


Fig. 7.—Graphical Representation of the Work Performed

work by addition of all the elements. Thus $W = \Sigma(p \Delta V)$. When the elementary steps are infinitesimally small, we obtain

$$W = \int p \, dV.$$

This equation may be transformed with the help of the equation of state $pV = \nu RT$ by substituting the value of $p = \nu RT/V$. We then obtain

$$W = \nu R \int T \frac{dV}{V}.$$

I. Isothermal Change.—In this case the temperature remains constant. Hence the last equation simplifies to

$$W = \nu RT \int_{V_1}^{V_2} \frac{dV}{V} = \nu RT (\log_e V_2 - \log_e V_1)$$

or
$$W = \nu RT \log_e \left(\frac{V_2}{V_1} \right).$$

From the equation of state we have

$$V_2 : V_1 = p_1 : p_2.$$

Hence we may also express the above equation in the form

$$W = \nu RT \log_e \left(\frac{p_1}{p_2} \right).$$

Work is performed by a gas when it expands against an external pressure. Hence the energy content of the gas is diminished by an equal amount. It follows, therefore, that the gas must cool down, unless heat is supplied to it from outside. This addition of heat must occur if the expansion is to be isothermal.

During (infinitely slow) isothermal expansion the gas merely plays the part of an agent whereby the heat supplied from outside is transformed into mechanical work. Since no other (internal) energy changes take place during the isothermal change of a perfect gas (experimental proof in next section), this transformation of heat into work is a complete one.

We can imagine the process to be realized as follows. The cylinder of fig. 6 is provided with a bottom which is perfectly permeable to heat, and stands the whole time in an infinitely large heat reservoir at constant temperature. The piston is in equilibrium when the pressure p , volume V , and constant temperature T satisfy the gas law $pV = \nu RT$.

Imagine now a virtual displacement of the piston, whereby V increases by ΔV and p decreases by Δp . If the piston is to be in equilibrium after the displacement, the load upon it must also be reduced by the amount ΔP . It must not be imagined, therefore, that the whole weight P is lifted throughout the isothermal process; on the contrary, P must be reduced after each elementary change.

The whole process is made up of a *succession of equilibrium states*. The increase of energy corresponding to the quantity of heat added in any element of time is just neutralized by the decrease of energy due to the raising of the weight. Thus the energy content of the gas remains constant throughout.

Now imagine the piston to be provided with an arrangement regulating the pressure automatically in such a way that the product pV remains constant at every instant during the change of position of the piston. The cylinder of gas could then take up an unlimited quantity of heat from the heat reservoir and transform it completely into mechanical work. Of course the cylinder would have to be infinitely long in order to take up an infinite quantity of heat from the reservoir. If the piston were driven back again, the work so performed would be transformed completely into heat, which would flow back once more into the heat reservoir at constant temperature. When eventually the piston had come back to its initial position, the distribution of energy between mechanical work and heat would be exactly the same as it was originally.

The amount of energy transformed alternately from heat into work and from work back into heat in this periodic process is given by the formula derived above,

$$W = \nu RT \log_e \left(\frac{V_2}{V_1} \right) = \nu RT \log_e \left(\frac{p_1}{p_2} \right).$$

Its value therefore depends upon the temperature at which the isothermal change takes place. Hence if we imagine an otherwise identical change to be carried out first at the temperature T_1 and then at the temperature T_2 , the ratio of the quantities of energy transformed will be

$$W_1 : W_2 = T_1 : T_2.$$

This opens up the possibility of transforming a greater quantity of energy from heat into work during the upward stroke of the piston than is transformed back again into heat during the downward stroke. For this purpose the upward stroke of the piston must take place at a higher temperature than the downward stroke, that is to say, a process must be inserted between the strokes whereby the temperature of the gas is alternately raised and lowered. Of course this new process must not require an extra expenditure of energy greater than the expected gain of mechanical work.

II. Adiabatic Change.—Here Poisson's law holds. We will make use of it in the form (p. 96) $TV^{\gamma-1} = C$ (where $C = \text{const.}$) in order to transform the general expression

$$W = \nu R \int T \frac{dV}{V}.$$

Taking logarithms on both sides of the above equation for Poisson's law, we obtain

$$\log_e T + (\gamma - 1) \log_e V = \log_e C,$$

whence
$$\log_e V = \frac{1}{(\gamma - 1)} \log_e C - \frac{1}{(\gamma - 1)} \log_e T.$$

Differentiation of this equation gives

$$\frac{dV}{V} = - \frac{1}{(\gamma - 1)} \frac{dT}{T}.$$

Substituting this in the equation for W we obtain

$$W = -\frac{\nu R}{(\gamma - 1)} \int_{T_1}^{T_2} dT = \frac{\nu R}{(\gamma - 1)} (T_1 - T_2).$$

This is the work performed by the gas during the raising of the piston. At the same time the gas cools from the temperature T_1 to the temperature T_2 . In the isothermal expansion the temperature was maintained at the initial value by the addition of a corresponding quantity of heat; but in the adiabatic change there is no addition of heat and hence the temperature fall is not neutralized. In the latter case all the boundary walls of the cylinder (including the bottom) must, of course, be completely impervious to heat.

The whole of the external work performed during an adiabatic change of a gas is derived from the energy content of the gas itself.

During the adiabatic expansion the pressure and volume are connected by the equation of Poisson's law, viz. $pV^\gamma = C$. The pressure also falls in this case when the volume is increased. In order that there may be equilibrium at every instant during the process by which a part of the energy contained in the gas is transformed into mechanical work, the load on the piston must be varied in accordance with Poisson's law. We will imagine as before that a suitable arrangement is fitted to the piston for this purpose. Then by raising the piston, a certain amount of the energy content of the gas can be withdrawn from it in the form of heat and transformed into mechanical work. The temperature of the gas is thereby lowered.

The lowest temperature which a body can have is that of the absolute zero. Hence if we put $T_2 = 0$, we shall obtain the total amount of energy which can be withdrawn from the gas. This is

$$W_{\max} = \frac{\nu RT}{\gamma - 1}.$$

By the Boyle-Gay-Lussac law $\nu RT = pV$; hence we may write the above expression in the form

$$W_{\max} = \frac{pV}{\gamma - 1}.$$

If we put the energy content of the gas at 0° abs. equal to zero (cf. § 14, p. 150), then W_{\max} represents the total energy content E at the temperature T . Thus we have

$$E = \frac{pV}{\gamma - 1}.$$

The total energy per unit volume of the gas, i.e. the *energy density*, is therefore

$$\frac{E}{V} = \frac{p}{\gamma - 1}.$$

If we imagine the piston to be alternately raised and lowered, there will be an alternate transformation of heat into work and work into heat. When the piston is displaced from an initial position and then returned to it again, the final distribution of energy between heat and work is also the same as at first. Hence it is impossible by means of a periodic process of alternate adiabatic expansions and compressions of a gas to withdraw heat continually from it in the form of mechanical energy.

It follows further from the main equation of p. 100 that:

The quantity of energy transformed during an adiabatic process is dependent only upon the difference of temperature between the initial and final conditions.

Applying this result to fig. 5, p. 100, it follows that the same quantity of energy is transformed when the gas passes from the condition A to the condition D by way of the adiabatic AD as when it passes from the condition B to the condition C by way of the adiabatic BC; for both AD and BC lie between the same isothermals, so that the initial and final temperatures are the same respectively in both cases.

6. Expansion of a Gas without Performance of External Work.

1. **Perfect Gases.**—In the imaginary experiment of ROBERT MAYER for the determination of the mechanical equivalent of heat (fig. 17, p. 30), the gas expands from the volume ABCD to the volume ABEF against the external pressure

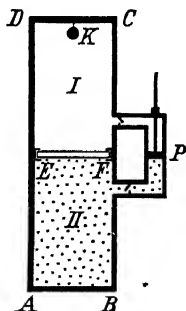


Fig. 8.—Expansion without Performance of External Work. Hirn's Apparatus

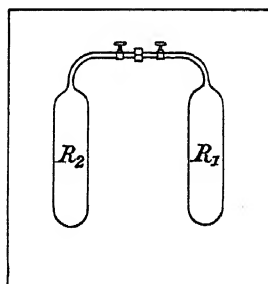


Fig. 9.—Joule's Experiment

of the atmosphere, thereby performing work. It is this work which accounts for the fact that a greater quantity of heat is required to raise the temperature of the air, and simultaneously to bring it into the volume ABEF, than is required merely to raise the temperature of the air by the same amount at the volume ABCD.

Imagine a closed cylinder ABCD (fig. 8) containing air and having an airtight glass partition EF across the middle. The two compartments are in communication through the pump P, by means of which all the air is pumped out of the compartment I into the compartment II. The whole apparatus is brought to a uniform known temperature in a calorimeter. The glass partition EF is now broken by allowing the iron ball K to fall down upon it. The air in II expands

without performing any work until it fills both I and II. This experiment was carried out successfully by HERN, who found that there was no change of temperature in the calorimeter.

JOULE performed the experiment with the following modification. He connected two equal metal cylinders R_1 and R_2 (fig. 9) by means of a tube fitted with a tap, and placed them in a vessel containing water which served as the calorimeter. The first cylinder R_1 was evacuated and the second R_2 filled with air under pressure. He then opened the connecting tap so as to allow a part of the air to flow from the second cylinder into the first. The compressed air thereby expanded to twice its original volume without doing any external work. JOULE observed no change of temperature in the calorimeter, from which it follows that the air neither absorbed nor gave out heat during the expansion.

The internal energy of a gas therefore remains constant when the volume changes (p. 34). This result may be expressed as follows:

The internal energy of a given mass of gas at constant temperature is independent of the volume.

According to p. 34 the internal energy is proportional to the absolute temperature.

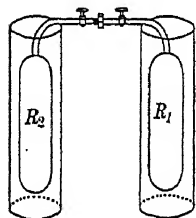


Fig. 10.—Joule's Apparatus

The above law is not at variance with the fact that a gas can perform mechanical work in expanding; for during expansion *with* performance of work the temperature falls, i.e. heat must be supplied from outside if the original temperature of the gas is to be maintained.

JOULE next proceeded to modify his experiment in the manner shown in fig. 10, namely, by placing the two cylinders in two similar but separate calorimeters and then opening the connecting tap. The water in the calorimeter containing R_1 (the originally evacuated cylinder) was heated, and the water in the other calorimeter was cooled. This is due to the fact that it is only in the first instant of its expansion out of R_2 that the air performs no work. As soon as there is air in R_2 , the subsequently entering air must overcome the pressure of that already present. *On the whole*, however, the temperature of the air did not change, i.e. no heat was developed or taken up. The total internal energy of the whole mass of air remained constant.

A similar experiment had been performed previously by Gay-Lussac and was taken by Robert Mayer as the basis of his calculation of the mechanical equivalent of heat (p. 28). Gay-Lussac worked without a calorimeter. His apparatus was similar to that shown in fig. 10, but each of the vessels was provided with a thermometer inside it. He observed that after equalisation of pressure the thermometer in the originally evacuated vessel had risen by the same amount as the other had fallen.

2. Real Gases.—It follows from the above experiments that there is no change of temperature when a perfect gas expands without performing external work. Accurate observation has shown, however, that there are considerable temperature changes when real gases are subjected to the same process.



Fig. 11.—Apparatus for the Demonstration of the Joule-Thomson Effect.

In 1852 JOULE and W. THOMSON repeated the experiments upon the expansion of gases without performance of external work, but with the following modification. The gas under investigation was compressed into a container and the pressure kept constant by means of a pump. The gas flowed out through a tube which was protected as efficiently as possible against loss and gain of heat. The pressure in the tube was also constant but lower than in the con-

tainer. In the tube (fig. 11) was a porous plug P of compressed silk or wool, through which the gas flowed slowly. The heat produced by friction in the plug was so small as to be negligible. After a time a stationary state was reached in which heat was neither absorbed nor developed. The temperatures of the gas in front of and behind the plug were then determined very accurately with the help of thermo-elements. A temperature difference was found. At one atmosphere difference of pressure this temperature difference amounted to about $-\frac{1}{4}^{\circ}\text{C.}$ for air, oxygen, and nitrogen, and about $-1\frac{1}{4}^{\circ}\text{C.}$ for carbon dioxide. In the case of hydrogen the change of temperature was very much smaller and of the opposite sign, there being a rise instead of a fall in temperature of about $+\frac{1}{40}^{\circ}\text{C.}$ as a result of the expansion. It was found that the temperature difference decreased in general with rise of initial temperature and vice versa (Joule-Thomson effect).

Experiment has shown that the Joule-Thomson fall in temperature ΔT is given by the equation

$$\Delta T = \mu \left(\frac{T_0}{T} \right)^2 \Delta p,$$

where Δp is the pressure difference, $T_0 = 273$, and T is the temperature of the experiment in degrees absolute. When $T = T_0 = 273^{\circ}\text{ abs.}$ the factor μ has the value 0.275 for air and 1.39 for carbon dioxide. Thus the temperature fall is inversely proportional to the square of the absolute temperature, i.e. the lower the temperature, the greater the temperature fall.

OLSZEWSKI succeeded later (1902) in showing that below -80.5°C. (the "inversion temperature") the behaviour of hydrogen also becomes normal, i.e. that below this temperature hydrogen is cooled down when it expands without performing external work. It has been found that there is an inversion temperature for every gas; the nearer the gas is to its condensation point at room temperature, the higher its inversion temperature. Hence the inversion temperature is particularly low in the case of helium, which boils at -269°C. under atmospheric pressure. In this case the inversion temperature is lower than that of liquid air.

The Joule-Thomson effect is made up of two processes. The first of these consists of forcing the gas through the porous plug and overcoming the back pressure of the gas already on the other side. The second process is the overcoming of the forces of cohesion during the expansion of the gas to the greater volume and lower pressure on the other side of the plug. At low temperatures the latter process predominates over the former, which generally causes a rise of temperature, so that the total Joule-Thomson effect is a temperature fall. In a perfect gas the second process does not exist, since perfect gases have no cohesion. In real gases, however, the cohesion makes itself apparent, its influence being greater, the nearer the gas is to its condensation point. These effects can be calculated from the van der Waals equation (see § 7, p. 90). Indeed the Joule-Thomson effects of different gases can be obtained very well from the van der Waals constants a and b . The Joule-Thomson effect is used very widely for the industrial liquefaction of air by the Linde method (especially in the production of nitrogen for the synthesis of ammonia).

7. Refrigerating Machines

1. Freezing Mixture.—The production of low temperatures by means of freezing mixtures has already been treated briefly on p. 70. The use of freezing mixtures (ice and common salt) for the preparation of ice cream depends upon the fact (p. 149) that a large quantity of heat is required by ice in melting (latent heat of fusion) and by salt in dissolving (heat of solution), i.e. by both substances

in becoming liquid. This heat is taken from the body placed in the freezing mixture.

2. Formation of Ice by Evaporation (p. 81).—This can be demonstrated by means of the apparatus shown in fig. 12. The flask-shaped bulbs A and B are connected by means of a horizontal tube and closed with singly bored stoppers. Through the stopper of A passes a thermometer; through that of B passes a tube with a tap and a funnel-shaped upper end. Both bulbs are partially filled with water, which is boiled by means of two flames. In this way all the air is driven out of the apparatus, which is then closed by means of the tap. All the water is now poured over into the bulb A. When now the flask B is dipped into cold water, the pressure of the water vapour in it is reduced by condensation to such an extent that the temperature in A becomes sufficient to make the water boil (§ 1, p. 81). A simultaneous fall of temperature is observed on the thermometer, since the water requires latent heat in boiling. The whole apparatus

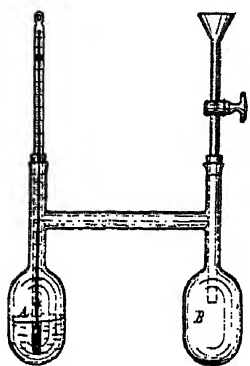


Fig. 12.—Formation of Ice by Evaporation

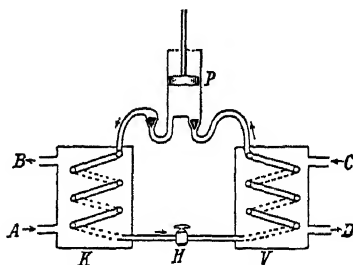


Fig. 13.—Carré Ice Machine (Diagrammatic)

having been brought down to room temperature in this way, all the water is poured over into A again. Concentrated sulphuric acid is then allowed to flow in slowly from the funnel. On account of the strongly hygroscopic nature of the sulphuric acid the water vapour within the apparatus is absorbed to a large extent, the sulphuric acid becoming warm. The water in A goes on developing water vapour by evaporation. Consequently its temperature goes on falling, in many cases getting as low as -10°C . (supercooling). Then ice formation sets in with simultaneous rise of temperature to 0°C .

The process of withdrawal of heat by evaporation finds wide practical application in the **Carré ice machine**.

Fig. 13 shows a diagrammatic sketch of such a machine. The pump P forces ammonia (or sulphur dioxide) gas into the spiral tube situated in the cooler K, and compresses it until it becomes liquid. The liquid is allowed to pass through the tap H into the other spiral tube on the right of the figure. It evaporates very rapidly and hence produces a great cooling effect. The heat required for the vaporization is taken from the bath V surrounding the spiral tube. The bath liquid is a concentrated salt solution (usually calcium chloride), whose temperature is thus reduced to -10°C . The cold bath liquid flows through a tube D into a vessel in which are placed pails containing water. Heat is withdrawn from this water, which therefore freezes. The bath liquid, whose temperature rises to 0°C ., is sent back again into the cooling bath V through the return tube C. The spiral tube in the jacket K is cooled by a stream of cold water, which enters through A and leaves at a higher temperature through B.

The process may also be regarded as a removal through B of the heat supplied through C. Obviously the heat is thereby raised from lower to higher temperature. In spite of this, however, the process is not at variance with the second law of thermodynamics (§ 9, p. 125); for in order that the process may be possible, the pump P must do work continuously during the refrigeration (p. 126).

By means of the Carré ice machine about 30 kg. of ice can be produced per hour per horse-power when the original temperature of the water to be frozen and the water of the cooler is 10° C.

The liquefaction of the constituents of the air already mentioned on p. 88 was carried out by PICTET in an apparatus consisting essentially of a combination of two refrigerating machines, in which the temperature lowering was produced by the evaporation of a liquid as in the Carré ice machine. In the first of these machines sulphur dioxide was liquefied by high pressure and cooling with cold water, and was then allowed to evaporate rapidly. In the evaporation vessel was a spiral tube in which carbon dioxide was cooled and liquefied by high pressure. The cold liquid carbon dioxide was then allowed to evaporate in another vessel in which was a tube containing the constituents of the air under pressure. A temperature of -130° C. was reached in this last cooling vessel. When the sulphur dioxide was replaced by nitrous oxide (N_2O), the temperature sank to -140° C. At this temperature and under high pressure the air became liquid.

The liquefaction of hydrogen was carried out by OLSZEWSKY in 1895 by compressing the gas to 190 atmospheres pressure and cooling it simultaneously with boiling oxygen (at a temperature of -211° C.).

3. The Linde * Refrigerating Machine.—This utilizes a quite different principle, namely, the fall of temperature accompanying the expansion of air without performance of external work (Joule-Thomson effect). The *counter current principle* is also applied in order to obtain a cumulative effect from a large number of successive expansions.

If air at 16° C. is compressed to 65 atmospheres and then allowed to expand to 22 atmospheres, then according to the numerical data given on p. 107 the temperature fall due to the Joule-Thomson effect is

$$\Delta T = 0.275(65 - 22) \left(\frac{273}{273 + 16} \right)^2 = 11^\circ \text{ C.}$$

The air therefore cools down to 5° C. If now this be used to cool a new quantity of compressed air, the temperature of the latter will fall by a further 11° C. when it is allowed to expand. Its final temperature will therefore be -6° C. Thus by repeated cooling and expansion of compressed air, the fall of temperature accompanying the expansion can be used each time to produce a further lowering of temperature. Indeed the lower the temperature, the more rapidly the temperature lowering takes place.

The construction of the Linde liquid air machine is seen in fig. 14. The air is drawn through the tube L into the double-barrelled pump C (the compressor), where it is compressed first to 22 atmospheres in the barrel *e* and then to 65 atmospheres in the barrel *d*. From here it flows through P_2 into the drying vessel *f*, and is cooled to 0° C. in the spiral tube *g* surrounded by ice. The compressed

* KARL VON LINDE, born 1842, Professor at Munich, published an account of his machine in 1895. At about the same time it became known that an Englishman HAMPSON had invented a machine working on the same principle.

and cooled air then enters the *counter-current apparatus* G. This consists of a long double-walled spiral tube packed round with wool to protect it against external heat. The compressed air enters at the top through the inner tube, whence it can pass at the bottom through the valve *a* into the outer tube. It thereby expands from 65 atmospheres to 22 atmospheres pressure and is cooled by 11°C . The air thus cooled to -11°C . flows back through the outer tube of the spiral in the opposite direction from that of the air in the inner tube. Thus the upward current is heated up and flows out through P_1 at 0°C ., while the

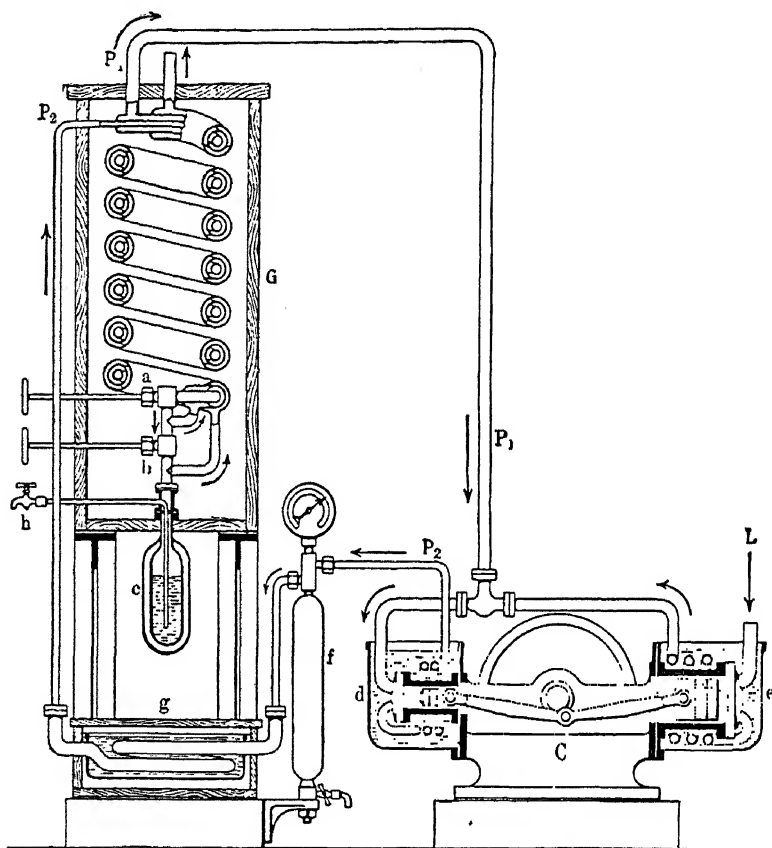


Fig. 14.—Linde Liquid Air Machine

downward current is cooled down so that it arrives at *a* with a temperature of -11°C . The air leaving through P_1 is compressed in the barrel *d* of the compressor, cooled down to 0°C . in *g*, and passes once more through the same process. Hence a continuous fall of temperature is produced in the counter current apparatus by the expansion at *a*. When the temperature has become so low that the air liquefies at a pressure of 22 atmospheres, it is allowed to run through the valve *b* into the flask *c*, whence it can be drawn off by means of the tap *h*. When the tap *b* is opened a part of the liquid air passing through it vaporizes at once, thereby lowering the temperature to -191°C ., the normal boiling-point. The air which has cooled down in expanding to atmospheric pressure flows round the counter-current apparatus in a tube completely surrounding the other tubes,

which are thus further cooled. The liquid air is collected in DEWAR flasks (figs. 8 and 9, p. 178). It can be kept for a considerable time in this kind of vessel; for the gradual evaporation of a part of the liquid keeps the temperature of the rest down to -191°C . Of course the Dewar flask must remain open, so that the liquid air can evaporate without danger of explosion.

Since air is made up of the two gases nitrogen and oxygen, liquid air is also a mixture of two liquids. Pure nitrogen boils at -195.7°C ., pure oxygen at -183°C . Thus nitrogen has a lower boiling-point than oxygen, whence it follows that fractional distillation takes place from an open Dewar flask containing liquid air, more nitrogen evaporating than oxygen. Hence liquid air gradually becomes richer in oxygen by evaporation. When 50 per cent of the liquid air has evaporated, the remainder contains 35 per cent oxygen; when 75 per cent has evaporated, the remainder contains 53 per cent oxygen.

This residual mixture, rich in oxygen, is widely used as an explosive in combination with organic substances such as wood charcoal. On account of the explosive nature of such a combination, caution is demanded in the use of liquid air for the cooling of vessels filled with wood charcoal (Vol. I, p. 326).

8. Cyclic Processes or Cycles

1. **General.**—Change of the condition of a body or system of bodies is often associated with a simultaneous change of the energy of the body or system, a part of this energy assuming some new form. The total energy, however, remains constant. Thus, for example, when a body falls from a certain height, a part of its potential energy is transformed into kinetic energy. If the body returns once more into its original condition, the energy also reassumes its original form and magnitude. In such a case the body is said to have performed a **cyclic process** or more simply a **cycle**.

As an example of a cyclic process we may quote the pendulum already treated in mechanics (Vol. I). Here the transformations of potential energy into kinetic energy and vice versa take place in regular alternation. If the motion of the pendulum is subject to no resistance, its amplitude remains constant. But in air the resistance of the medium decreases the amplitude and causes an apparent loss of energy. In reality, however, the pendulum has given up a part of its energy to the air. In this case we say that the system formed by the pendulum alone is not a *closed* system, since other bodies (the air) not actually belonging to it also take part in the transformation process.

In a cyclic process a part of the energy may be transformed into *thermal energy*. At the end of the closed cyclic process, however, this thermal energy must have been changed back into its original form.

As an example of such a closed cyclic process we may take the adiabatic change of condition of a gas contained in a vessel with walls impervious to heat (p. 101). When the gas is brought back to its original condition, the energy also reassumes its original form.

In expanding isothermally a gas absorbs heat energy from the heat reservoir (p. 103), though the latter is external to the system actually performing the process. In returning isothermally to its original condition the gas gives up to the reservoir the heat energy which it previously absorbed. Thus the total process can be called a cycle, although the energy content of the body was changed temporarily during it. If the system be taken to include the heat reservoir as well as the gas, then the whole forms a closed system which performs a cyclic process with constant total energy.

In the examples mentioned above the process by which the energy was transformed back to its original form was the exact reverse of the first half of the cycle. This is not absolutely necessary, however, since energy is a scalar quantity and independent of the path.

Consider, for example, a sphere inside a ring-shaped tube at its highest point. When released, the sphere falls down one side of the ring and rises up the other side again to its original position. In this case there is again a transformation of potential energy into kinetic energy and a complete reverse transformation; but the path of the first half of the process is different from that of the second.

When the above sphere has regained its original position, the condition of the system is exactly as it was at the beginning of the cyclic process. Thus the mechanical process of the falling of the sphere is reversible.

In general, a process is said to be **reversible** when the original condition of the system can be fully restored in any manner and by any means, i.e. restored so that *all* of the bodies taking part in the process are brought back to their original conditions. If such a reversal is impossible, the process is said to be **irreversible**.

Thus for the characterization of a process as reversible it need not necessarily be capable of reversal in the sense that the second half of the closed cycle is identical with the first, but in the opposite direction. A process is to be regarded as reversible, provided that the whole of the system taking part in it can be made to reassume its original condition in any way whatever. If there is no way in which this is possible, then the process is irreversible (p. 123).

When a body or a part of the system taking part in a process comes back to its original condition, we say that that body or that part of the system has performed a *cyclic process*. During this cyclic process the condition of other parts of the system may have changed. If now all these other parts of the system reassume their original condition when the cyclic process of the one body or one part of the system is reversed, then we have a *reversible cyclic process* or a *reversible cycle*. The consideration of such reversible cycles plays a great part in thermodynamics.

It is not possible to give in advance a general experimental criterion as to whether a process is reversible or not.

In order to grasp the difference between a reversible and an irreversible process, let us consider the case of a steel ball falling on to a plate.

At the beginning of its fall the ball possesses a certain potential energy corresponding to its position. This potential energy is transformed completely into kinetic energy during the fall. Now imagine the ball to impinge upon a horizontal, perfectly elastic steel plate. As a result of the impact the kinetic energy of the ball is transformed instantaneously into potential energy of the elastic deformations of both bodies. Then follows an immediate recovery from these deformations, and the ball rebounds from the steel plate with the same kinetic energy as it had before impact. As it rises this kinetic energy is transformed back again into potential energy. At the moment when the ball reaches its original position, its energy also reassumes its original form. Every individual part of the system has returned of itself to its original condition. The process is a purely mechanical one and, like all such, is reversible in every detail. The same is true of all purely electromagnetic processes.

If, on the other hand, the ball falls upon an inelastic lead plate, its kinetic energy is transformed into heat by friction during the deformation of the lead. In this case there is no reverse transformation of the heat energy; on the contrary, the heat developed at the point of impact distributes itself uniformly throughout the whole of the lead plate, eventually causing a uniform rise of temperature. Thus the process does not reverse itself; and there is no means by which the dissipated heat energy can be concentrated again and transformed back so as to make the ball rise up again from the plate. The process takes place in one direction, but never in the other: it is irreversible.

A process becomes irreversible as soon as it ceases to be purely mechanical in the usual sense of the word, i.e. as soon as there is friction and consequent production of heat. In the same way reversible electromagnetic processes become irreversible as soon as imperfect conductors or insulators give rise to the production of heat by the currents in a manner analogous to the production of frictional heat in mechanical processes. Now strictly speaking no terrestrial mechanical process is frictionless and no terrestrial insulator or conductor is perfect. Hence all mechanical and electrical processes are really irreversible and their reversibility is only an abstraction, though an abstraction which often corresponds very nearly to actual fact. There are also other irreversible processes besides that of friction.

In a closed system, i.e. a system in which there is no loss or gain of total energy, certain processes can take place spontaneously or as the result of a mere release, such as the opening of a tap, the bringing of two bodies into contact with one another, the making of an electrical contact, and the like. All such processes are irreversible.

Examples.—Equalization of pressure in a gas, equalization of temperature by conduction or radiation, equalization of concentration by diffusion, &c. A closer consideration of these processes reveals the fact that, in order that they may proceed with finite velocity, one parameter must always be indeterminate. Thus the opening of the tap of a vessel containing gas under pressure or the release of a piston so that the gas drives it out rapidly against a lower external pressure gives rise to a *turbulent* motion in which the pressure of the gas is indeterminate. In such cases therefore it is impossible to determine the work performed by the gas from the expression $\int p dv$. This would only be possible if the gas were allowed

to expand infinitely slowly in infinitesimally small pressure stages, for instance by establishing successive pressure equilibria with an infinitely large number of containers each of which had an infinitesimally lower pressure than the one before it, or by removing the load from the piston (p. 103) by infinitesimally small steps. Such methods would allow of an infinitely gradual reduction of the pressure of the gas. The expansion would then be reversible; for in order to reverse the whole process it would only be necessary to bring the vessel containing the gas into successive equilibria with the containers in the reverse order, or gradually to increase the load on the piston again to its original value. The same reversibility could also be attained in the case of thermal conductivity or radiation. The pressure containers would then have to be replaced by heat reservoirs with graduated temperatures and the body brought into temperature equilibrium with each of them in succession.

From what has been said above it follows that a reversible process can only take place infinitely slowly, so that the system is always in *pressure or temperature equilibrium* or in a condition deviating only infinitesimally from such equilibrium. In this case the pressure and temperature (and also concentration, &c.) have definite values at every instant. In actual fact processes may occur fairly rapidly and yet remain very nearly reversible. For example, a gas may flow comparatively rapidly, because its individual particles themselves have very great velocities and thus establish the definite pressure very quickly. When occasioned by finite differences of pressure or temperature, a *spontaneous* process is always irreversible; but with the help of special devices and controls it may be *conducted* reversibly.

The spontaneous reversal of irreversible processes is not absolutely *impossible*, however; but it is so *improbable* that it may be regarded as impossible for all practical purposes (BOLTZMANN*). The reason for this is to be found in the complex structure of the matter involved, which consists of an immense number of individual atoms and molecules. In the investigations of physical processes, account must be taken of the motions of these ultimate particles and the distribution of velocities amongst them. The explanation of all phenomena on the basis of these elementary motions is the problem of so-called *statistical mechanics*.

Consider a vessel divided into two compartments A and B and containing two particles x and y in random motion. Then there are four possible and equally probable states, namely (i) x in A and y in B, or (ii) y in A and x in B, or (iii) x and y in A, or (iv) x and y in B. Thus the probability of both particles being in A is $\frac{1}{4}$. If we have three particles, the probability of all being in A and none in B is considerably smaller. With increasing number of particles the probability of this state decreases very rapidly, becoming vanishingly small when the number of particles is very large. The smaller the probability of an event, the longer the average time that elapses before it happens. Now in the case of a gas we are dealing with an immense number of individual molecules; hence there is only a vanishingly small probability that the average uniform distribution of the molecules in a relatively large volume will show a chance disturbance great enough to be recognizable with an extremely rapidly acting manometer. Such momentary compressions or rarefactions may well occur in very small volumes; but on

* LUDWIG BOLTZMANN (1844–1906), whose acute and fundamental researches led him to become one of the founders of the kinetic theory of gases. He was Professor of Theoretical Physics, chiefly at Vienna.

account of the rapidity of the molecular motions their duration must be very short. What we measure with a manometer is the space and time average over a large volume and (even with very rapidly acting pressure gauges) over a relatively long time. The probability of the occurrence of a momentary state in which there is an abnormal concentration of gas molecules in one part of a given volume may be compared to the probability of throwing a large number of dice so that they all show 6, or the probability of obtaining the text of this book by shaking letters in a line out of a large sackful. The above cases are quite possible, but they are extremely improbable (see below). As with gaseous pressure, so also with temperature distribution. There is only a vanishingly small probability of a momentary chance excess of the more rapidly moving molecules in one part of a comparatively large volume, i.e. of the appearance of a difference of temperature between different parts of the gas. The probability of the persistence of such a temperature disturbance for a time long enough to permit of its being measured is of an even higher order of smallness (cf. § 1, p. 39 and § 2, p. 56).

Thus we see that in the cases of pressure and temperature equalization and also of concentration equalization by diffusion, which we designate as irreversible processes, reversal is not impossible but extremely improbable. *A process may be taken as irreversible when its reversal is almost infinitely improbable.*

2. Carnot's Cycle.—The mighty quantities of energy which are indispensable to modern life were first made available by means of heat engines (e.g. the steam-engine). In these engines the heat energy of the process of combustion is transformed into mechanical energy. Very soon after the discovery of the steam-engine it was recognized that it only transformed a fraction of the total heat energy in this way. Repeated efforts have therefore been made to increase the efficiency of heat engines (i.e. the ratio of the output of mechanical energy to the total heat energy) as much as possible. SADI CARNOT was the first to calculate (1824) on theoretical grounds the maximum efficiency of an ideal heat engine. The Carnot cycle is therefore of fundamental importance for the development of the theory of heat engines.

It was shown on p. 102 that an infinitely large quantity of heat energy could be transformed into mechanical work by the isothermal expansion of a gas into an infinitely long cylinder. Since, however, it is impossible to make an engine with an infinitely long cylinder, it follows that only a finite quantity of heat can be transformed into mechanical work by the isothermal expansion of a gas. The quantity of work obtainable is given by the equation

$$W = \nu RT \log_e \left(\frac{V_2}{V_1} \right),$$

which shows that not very much heat can be transformed into work unless a very long cylinder be used. In order to produce a sufficient quantity of mechanical work for practical purposes, the piston enclosing the gas must therefore be brought back repeatedly into its original position, and the total output of work increased by repetition

of the isothermal expansion with the help of a periodically acting device.

But the mechanical work produced in the expansion is used up again completely in compressing the gas isothermally back to its original condition. Thus at the end of the whole process we have exactly the same quantity of heat as at the beginning and the method is useless as a means of producing mechanical work.

It was mentioned on p. 103, however, that mechanical work can be gained by compressing the gas at a lower temperature than that at which it expanded. It was also stated that the quantity of heat energy transformable into mechanical work by isothermal expansion is proportional to the absolute temperature of the gas. Upon these principles is based the following (ideal) heat engine (fig. 15) (Carnot's cycle).

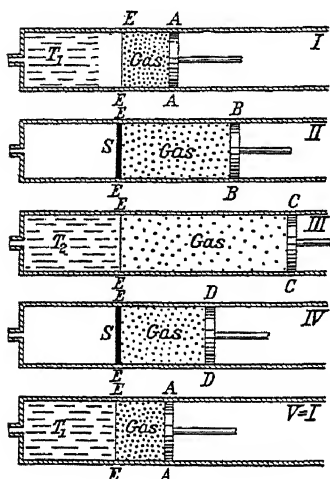


Fig. 15.—Carnot's Cycle

A certain mass of gas is enclosed in a cylinder by means of an easily movable piston. The piston and the cylinder walls are completely impervious to heat, but the end EE of the cylinder is a perfect thermal conductor. This end is placed in contact with a heat reservoir which can be kept at constant temperature. The perfectly conducting end of the cylinder may also be covered with a disc S made of material which is completely impervious to heat. Fig. 15 shows the engine and heat reservoir in five successive conditions. The fifth is identical with the first; the gas therefore passes through a complete cyclic process.

In the first phase the heat reservoir is kept at the temperature T_1 and the gas, whose original volume is V , expands isothermally, thereby moving the piston AA to the right and performing external work. The requisite energy is supplied to the gas in the form of a quantity Q_1 of heat from the heat reservoir at temperature T_1 . The pressure exerted by the gas upon the piston, and transmitted farther by the piston rod, decreases gradually according to the equation of state $pV = \nu RT_1 = \text{const.}$ The piston eventually reaches the position BB (II).

The end of the cylinder in contact with the heat reservoir is now covered with the disc S of material impervious to heat. From this point onwards the gas expands *adiabatically* and its temperature therefore falls to T_2 , by which time the piston has taken up the position CC (III). The work performed by the gas in this phase is derived from its own internal energy.

The heat reservoir is now kept at the temperature T_2 assumed by the gas as a result of its adiabatic expansion, and the disc S is removed so as to render the end of the cylinder perfectly conducting once more. The piston is then driven into the cylinder by the application of external work, but in such a way that there is equilibrium between the force upon the piston and the thrust of the gas upon it. If the end of the cylinder were impervious to heat, this compression would cause the temperature of the gas to rise. But as it is, a quantity Q_2 of heat equivalent to the work done upon the gas flows at temperature T_2 into the heat reservoir. The piston thus reaches the position DD (IV).

The end of the cylinder is now covered once more with the non-conducting disc S , and the gas compressed adiabatically until the piston returns to its original position AA ($V = I$). The position DD (IV) must be chosen in such a way that the temperature of the gas reassumes the value T_1 at the end of the whole cycle when the piston has returned to AA . The mechanical work performed upon the gas in the adiabatic compression then raises its temperature to the original value and the whole cyclic process can be repeated.

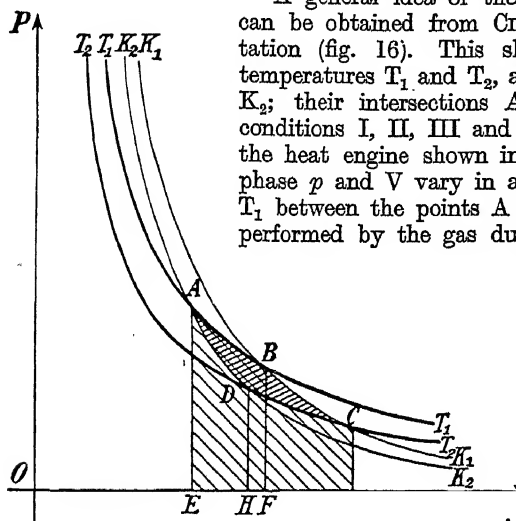


Fig. 16.—Isothermals and Adiabatics in Carnot's Cycle

the figure $CDHG$, bounded above by the isothermal T_2 , represents the external work done upon the gas. Then follows the last phase, the adiabatic compression from D to A . The external work done upon the gas in this compression is represented by the area of the figure $DAEH$ which is bounded above by the adiabatic K_2 .

On the whole, the excess of the work done by the gas over the work done upon it during the complete cycle is represented by the area of the figure $ABCD$ bounded by the four arcs of the isothermal and adiabatic curves. The cycle is thus accompanied by a gain of mechanical work. The requisite energy is derived from the excess of the quantity Q_1 of heat absorbed at the higher temperature T_1 during the motion of the piston from AA (I) to BB (II) over the quantity Q_2 of heat given back to the heat reservoir at the lower temperature T_2 during the return of the piston from CC (III) to DD (IV).

The amounts of work performed by the gas in the different phases of the cycle may be calculated from the equations derived in § 5, pp. 102 and 104. For the sake of simplicity we will measure in mechanical units the quantities of heat taken from and given back to the heat reservoir. These can then be transformed afterwards into thermal units. We will designate the volume and pressure of the gas for each of the piston positions AA , BB , &c., by corresponding subscripts,

e.g. p_A , V_A , &c. The amounts of work performed during the different phases will also be designated by subscripts; thus, for example, W_{AB} will represent the work done by the gas during the displacement of the piston from the position AA to the position BB.

In the first phase AB (fig. 16) of the process a certain quantity of heat $+Q_1$ is supplied to the gas at the temperature T_1 . The gas performs an amount of work equivalent to this quantity of heat, viz. (p. 102)

$$W_{AB} = \nu R T_1 \log_e \left(\frac{V_B}{V_A} \right).$$

In the second phase BC of the process a portion of the internal energy of the gas is transformed into mechanical work without external supply of heat. The gas performs the work (p. 104)

$$W_{BC} = \frac{\nu R}{\gamma - 1} (T_1 - T_2)$$

and its temperature falls from T_1 to T_2 .

The third phase consists of an isothermal compression of the gas from C to D by the expenditure of external mechanical work upon it. If it were to *expand* isothermally from D to C, the gas would do the work

$$W_{DC} = \nu R T_2 \log_e \left(\frac{V_C}{V_D} \right).$$

Conversely, when this amount of work is done upon the gas, as is the case during the compression from C to D, the work performed by the gas must be

$$W_{CD} = \nu R T_2 \log_e \left(\frac{V_D}{V_C} \right),$$

which, as is seen from the logarithm, has a negative value. At the same time a quantity of heat Q_2 equivalent to W_{CD} flows out of the gas into the heat reservoir at T_2 . The quantity of heat supplied to the gas is therefore $-Q_2$, the negative sign indicating that the gas actually loses heat.

In the fourth phase DA the volume of the gas is diminished adiabatically. The mechanical work done in moving the piston from DD to AA goes to increase the internal energy of the gas and raise its temperature to the original value T_1 . In expanding adiabatically from A to D (and simultaneously cooling from T_1 to T_2) the gas would perform the mechanical work (p. 104)

$$W_{AD} = \frac{\nu R}{\gamma - 1} (T_1 - T_2).$$

But in the fourth phase the gas is compressed, i.e. this amount of work is done upon it. The work actually done by the gas during the compression is therefore negative and equal to

$$W_{DA} = \frac{\nu R}{\gamma - 1} (T_2 - T_1).$$

There is no gain or loss of heat during this phase.

The value of W_{DA} is equal to that of W_{BC} but of opposite sign. This is to be expected, since the amount of work associated with an adiabatic change depends only upon the temperature difference (p. 105), and this is the same in both cases. The net gain of mechanical energy is therefore equal to the difference between the absolute values of W_{AB} and W_{CD} . This is obtained by adding the values

obtained above, which already include the proper signs. On the whole, therefore, the gas has performed the mechanical work

$$W = W_{AB} + W_{BC} + W_{CD} + W_{DA} = W_{AB} + W_{CD}.$$

This net output of work is equivalent to the net quantity of heat supplied,

$$Q = Q_1 - Q_2.$$

Of the latter $|Q_1|$ is absorbed at the temperature T_1 and $|Q_2|$ given up again at the lower temperature T_2 . According to the first law of thermodynamics the quantities Q and W must be equivalent, i.e. we must have

$$W = JQ.$$

This can also be seen at once from the individual terms of the sums for W and Q . The value of W may be transformed as follows:

$$\begin{aligned} W &= W_{AB} + W_{CD} = \nu RT_1 \log_e \left(\frac{V_B}{V_A} \right) + \nu RT_2 \log_e \left(\frac{V_D}{V_C} \right) \\ &= \nu RT_1 \log_e \left(\frac{V_B}{V_A} \right) - \nu RT_2 \log_e \frac{V_C}{V_D}. \end{aligned}$$

Now by Poisson's law

$$V_A \gamma^{-1} T_1 = V_D \gamma^{-1} T_2 \quad \text{and} \quad V_B \gamma^{-1} T_1 = V_C \gamma^{-1} T_2,$$

whence by division we have
$$\frac{V_B \gamma^{-1}}{V_A \gamma^{-1}} = \frac{V_C \gamma^{-1}}{V_D \gamma^{-1}},$$

i.e.
$$\frac{V_B}{V_A} = \frac{V_C}{V_D}.$$

Combining this with the expression for W obtained above we have

$$W = \nu R (T_1 - T_2) \log_e \left(\frac{V_B}{V_A} \right).$$

The ratio of this net gain of work to the heat energy W_{AB} taken by the gas from the reservoir at T_1 is therefore

$$\frac{W}{W_{AB}} = \frac{T_1 - T_2}{T_1}.$$

This is the ratio of the output of work from the engine to the heat supplied to it at the temperature T_1 .

During the process a part of the heat supplied flows back into the heat reservoir at the lower temperature T_2 . Its quantity $-Q_2$ is determined by the expression for W_{CD} , and its ratio to the quantity of heat supplied at T_1 is at once obtained by division, viz.

$$\frac{-W_{CD}}{W_{AB}} = \frac{T_2}{T_1}.$$

So far we have expressed the energies in mechanical units. In order

to transform to thermal units, we simply have to multiply by the factor K (p. 32). Hence

$$Q_1 = KW_{AB} \quad \text{and} \quad -Q_2 = KW_{CD}.$$

The ratios of the energies are not affected by this change of units. We can therefore write at once

$$\frac{Q_1 - Q_2}{Q_1} = \frac{W}{W_{AB}} = \frac{T_1 - T_2}{T_1} \quad \text{and} \quad \frac{Q_2}{Q_1} = \frac{-W_{CD}}{W_{AB}} = \frac{T_2}{T_1}.$$

This final result may be expressed as follows:

By means of Carnot's cycle the energy of a quantity of heat withdrawn from a heat reservoir at the higher temperature T_1 may be divided into two fractions μ and $(1 - \mu)$, the first of which is obtained as mechanical work, while the second flows back into a heat reservoir at the lower temperature T_2 . These fractions are given by the quotients $\mu = (T_1 - T_2)/T_1$ and $(1 - \mu) = T_2/T_1$.

The quotient μ is called the **thermal efficiency** of the process.

As treated above, the Carnot cycle consists of a *succession of states of equilibrium*; it must therefore take place infinitely slowly. In particular we have assumed that no temperature difference arises between the gas and the heat reservoir in the two isothermal phases. The calculations are only valid if this is the case.

In accordance with the considerations put forward in the previous paragraph it follows therefore that the whole cyclic process can also take place in the reverse direction. Thus Carnot's cycle is a reversible process. When it is conducted in the reverse direction, we get the following result:

By the absorption of a quantity Q_2 of heat from a heat reservoir at the lower temperature T_2 and the expenditure of an amount $J(Q_1 - Q_2)$ of external work upon the gas, it is possible to supply a quantity Q_1 of heat to a heat reservoir at the higher temperature T_1 .

The fundamental principle of the reversed Carnot cycle finds application in refrigerating machines (§ 7, p. 107). The working gas only performs a true cycle if it reassumes its original condition completely. The heat reservoirs alter its condition, in that the first one supplies heat and the other removes it partially. The system, gas + heat containers, only completes a cyclic process after passing through the Carnot cycle twice, once in the forward direction and then back again in the reverse direction. Assuming infinite slowness, everything has then returned to its original condition.

3. Generalization of the Principle of Carnot's Cycle.—Carnot's cycle is of particular importance because the thermal efficiency of an ideal heat engine was first calculated by means of it. But this efficiency is by no means confined to the Carnot cycle. On the contrary every heat engine performing a reversible cyclic process has exactly the same efficiency. It makes no difference whether the working substance is a gas, a vapour, a liquid, or a solid, provided only that the process is reversible, i.e. that it consists of a succession of equilibrium states.

1. The fact that every heat engine in which a working substance performs a reversible process must have the same efficiency $\mu = (T_1 - T_2)/T_1$ can be proved as follows:

Consider any two reversible heat engines M and N working between the temperatures T_1 and T_2 . Suppose that M has the efficiency $a\mu$, whereas N only has the efficiency μ . Then by means of M it would be possible to absorb a quantity Q of heat from a hot reservoir, transform a part $a\mu Q$ of it into mechanical work and return the rest $(1 - a\mu)Q$ to a cold reservoir. The second heat engine with the smaller efficiency could be allowed to work in the reverse direction in combination with the same reservoirs in such a way as to require the expenditure of the same amount $a\mu Q$ of external work as was developed by M. Since the efficiency of N is μ , it would deliver the quantity aQ of heat to the hot reservoir and absorb the quantity $a(1 - \mu)Q$ of heat from the cold reservoir. The former quantity is made up of the latter together with the thermal equivalent $a\mu Q$ of the work expended upon the engine.

The result of the total process performed by both engines in combination would therefore be as follows. The mechanical work involved would be zero. More heat would have been taken from the cold reservoir than would have been supplied to it. This excess $(a - 1)Q$ would be equal to the excess of the heat supplied to the hot reservoir over the heat taken from it. On the whole, therefore, heat would have passed from the cold to the hot reservoir without the expenditure of external work. This is not at variance with the *first law of thermodynamics*, but it is certainly contrary to *experience*. It has never been found possible by any means whatever to withdraw heat from a heat reservoir at lower temperature and transfer it to a heat reservoir at higher temperature without the expenditure of work or the simultaneous occurrence of some other changes.

In the above example the second engine N might also be allowed to work in such a way as to supply the heat reservoir with a quantity of heat Q equal to that withdrawn by the engine M, so that this reservoir would return to its original condition. An amount of work μQ would then have to be done upon the engine N. Simultaneously the quantity of heat $(1 - \mu)Q$ would have to be withdrawn from the cold reservoir. But this is greater than the quantity $(1 - a\mu)Q$ of heat which would be given up to the cold reservoir by the engine M. Hence the result of the combined action of the two engines would be to leave the hot reservoir in its original condition and completely to transform the heat withdrawn from the cold reservoir into an equivalent amount $\mu Q(a - 1)$ of work. This has also been found *by experience* to be impossible.

It is impossible to construct a device which will withdraw heat from sea water, for example, and transform it completely into useful

work. Since the natural stores of heat are inexhaustible, such an engine would have an immense supply of energy. It would therefore represent a type of perpetual motion machine not excluded by the first law of thermodynamics. This type of perpetual motion machine is said to be of the *second kind* to distinguish it from the *first kind* forbidden by the first law.

The principle of the impossibility of a perpetual motion machine of the second kind, also known as the second law of thermodynamics (§ 9, p. 125), is based entirely upon experience. A necessary deduction from it is that every reversible heat engine, no matter what its working substance, must have the same efficiency μ as an engine employing a perfect gas and working between the same temperatures. Thus the efficiency of every reversibly working engine is that calculated by CARNOT, viz.:

$$\mu = \frac{T_1 - T_2}{T_1}$$

The thermal efficiency

$$\mu = \frac{T_1 - T_2}{T_1} = 1 - \frac{T_2}{T_1}$$

of a reversible heat engine is proportional to the difference $T_1 - T_2$ between the initial and final temperatures of the process. Hence the greater this difference, the more favourable the working conditions. The temperature of the hotter heat reservoir must therefore be made as high as possible and that of the colder one as low as possible. The efficiency would become equal to 1 if the temperature T_2 of the colder reservoir could be made equal to that of the absolute zero (see below).

When we come to consider actual heat engines we shall find that these theoretical results are borne out by practical experience. In a steam engine, for example, the efficiency may be increased by raising the temperature of the steam entering the cylinder and by lowering the temperature of the condenser into which the steam escapes after it has performed its work.

II. In the graphical representation Carnot's cycle corresponds to a four-sided closed figure bounded by the arcs of two isothermals and two adiabatics. But any other closed figure, no matter how complicated, also represents a reversible cycle, provided that the fundamental conditions are the same as for Carnot's cycle.

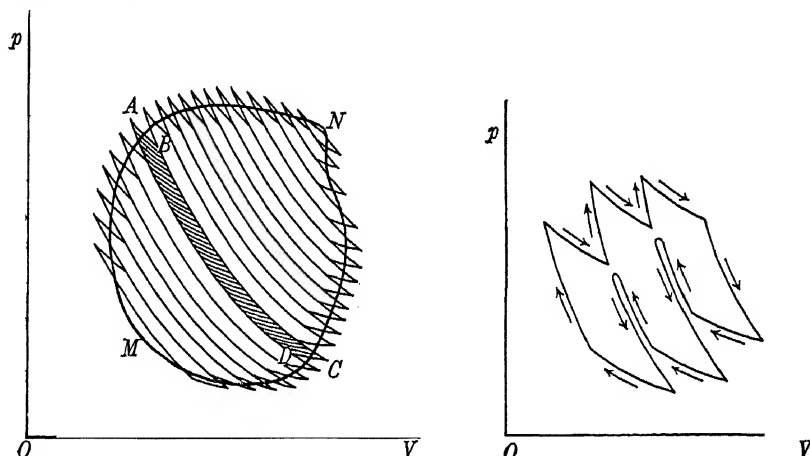
Imagine such a process represented by a closed curve of any shape, e.g. by the curve MANC in fig. 17. We may divide up the enclosed area into a very large number of elementary areas, each lying between neighbouring adiabatics and bounded at the ends by isothermals. An example of such an element of area is that enclosed by the adiabatics AD and BC and the isothermals AB and DC in the figure. In passing through the conditions represented by the periphery of this element, the gas performs a Carnot cycle. Now imagine the gas to perform all these elementary cycles in succession in the manner indicated diagrammatically in fig. 18. The changes corresponding to points inside the zigzag boundary

cancel out and we are left with the changes corresponding to a passage round this boundary alone. Now the smaller each element of area is chosen, the more nearly the zigzag approximates to the original boundary curve (fig. 17). In order actually to conduct such a process it would be necessary to supply or withdraw a quantity dQ of heat at each element of arc corresponding to passage along an isothermal. Each of these elementary quantities of heat would have to be supplied or withdrawn at the temperature of the corresponding isothermal. When this condition is fulfilled, the gas performs a reversible cyclic process. Hence:

All reversible cyclic processes have the same thermal efficiency

$$\mu = \frac{T_1 - T_2}{T_1}.$$

If there were any reversible cycle for which this is not true, it would always be possible to combine that cycle with a Carnot cycle



Figs. 17 and 18.—Cyclic Processes

working with the same heat reservoirs in such a way that the combined cycles would give a result at variance with the second law of thermodynamics (i.e. either production of work from a store of heat at constant temperature or transference of heat from a lower to a higher temperature without expenditure of external work).

A number of conditions must be fulfilled in order that a cyclic process may be reversible. They can be summed up in the one condition already referred to several times above, namely, that the process must consist of a succession of states of equilibrium. From this follows further: (1) There must be no loss of heat by conduction away through the walls of the cylinder. (2) At no point of the process may finite differences of temperature occur; for this would result in equalization of temperature, with the result that a part of the difference ($T_1 - T_2$), which determines the thermal efficiency, would be lost without production of work. (3) The external pressure determining the work done must never differ by more than an infinitesimal amount from the pressure of the gas.

These conditions can never be realized in actual fact. Hence Carnot's cycle is the *ideal* case of a heat engine. The thermal efficiency calculated from it is

therefore the maximum possible for a heat engine; we can approach this maximum, but never attain or exceed it. Every deviation from the above conditions (1) to (3) results in a loss of heat without production of mechanical work and a loss of reversibility on the part of the engine.

Irreversible cyclic processes therefore have a smaller thermal efficiency than reversible ones.

4. **The Kelvin or Thermodynamical Scale of Temperature.**—It was pointed out on p. 5 that the original definitions of temperature by means of a mercury or hydrogen thermometer are completely arbitrary. They provide no guarantee that the concept of temperature so defined does not involve peculiarities of the particular thermometric substance of which it ought to be independent. Now the simple relation $Q_1/Q_2 = T_1/T_2$, derived on p. 120 for the quantities of heat taken in and given out during a reversible cycle, is certainly quite independent of any material properties of the working substance. Careful measurements also prove that the relation is not satisfied if T_1 and T_2 are measured by a mercury thermometer from -273°C. (or more accurately -273.2°C.) as zero (see the table on p. 6). The same is true when the hydrogen thermometer is used to measure the temperatures, though in this case the deviations from the theoretical are different. The deviations in both cases must be due to the lack of a satisfactory thermometer, i.e. to the fact that the coefficient of expansion of mercury and the pressure coefficient of hydrogen are not independent of the temperature.

This difficulty was removed by a proposal of W. THOMSON (LORD KELVIN).^{*} His proposal was to use the above equation itself to determine temperatures on a *thermodynamical scale*. In accordance with the first law of thermodynamics, the ratio Q_1/Q_2 of the quantities of heat involved in a cyclic process may be obtained by measuring the equivalent energies. Thus it is possible in this way to determine the ratio of two temperatures just as easily as the ratio of two volumes of a given mass of mercury.

The small deviations found by experiment between the thermodynamical scale and the mercury or hydrogen scale are to be regarded as corrections to the latter arising from the slight lack of uniformity in the expansion of these thermometric substances. With increasing rarefaction the individual properties of all gases become less marked, and their obedience to the Boyle-Gay-Lussac law more nearly exact. Hence in the limiting case of infinite rarefaction the behaviour of a real gas may be taken as identical with that of a perfect gas. Now the reversible cycle is an ideal process only realizable with a perfect gas. The thermodynamically determined temperature is therefore identical with that which would be indicated by a thermometer containing a gas at infinite rarefaction.

Since a perfect gas does not exist, the determination of temperature thus indicated is always accompanied with a certain degree of uncertainty, the limits of which are determined by the level of experimental technique. The thermodynamical definition of temperature opens up the possibility of unambiguous determinations in all regions of temperature, including those in which it is impossible for practical reasons to work with gas thermometers. Thus all gases liquefy at very low temperatures; and since all solids melt at very high temperatures, no terrestrial material exists in which a gas could be confined under these conditions. In the theory of radiation, however, certain temperature laws have been deduced (Vol. V) from the *second law of thermodynamics*, which is

^{*} SIR WILLIAM THOMSON (1824–1907, from 1892 onwards LORD KELVIN), Professor of Physics in Glasgow. His highly original methods of treatment enabled him to make important advances in the most varied branches of physics.

itself based on Carnot's cycle. These laws permit certain conclusions as to thermodynamical temperatures to be drawn from the results of practicable experiments. In this way methods are opened up for the direct and absolute measurement of temperatures lying right outside the regions in which expansion thermometers are applicable.

9. The Second Law of Thermodynamics

1. The First Law of Thermodynamics.—We have seen above that mechanical work can always be converted completely into heat. The first law of thermodynamics (§ 9, p. 32) states that to every quantity of work expended there is a definite equivalent quantity of heat. Hence work can never be lost during the process of conversion; there is always an equivalent quantity of heat produced. The first law is the principle of the conservation of energy, applied to thermal processes.

2. The Second Law of Thermodynamics.—I. We have also seen that heat can be converted into mechanical work and that the conversion always takes place in accordance with the energy principle, the work obtained being equivalent to the heat supplied. But this process can never take place alone; it must necessarily be accompanied always by other permanent changes of condition. In the case of an engine working periodically in a cyclic process, these changes consist of a transference of heat from a reservoir at higher temperature to another at lower temperature. In addition to supplying the useful quantity of heat which is converted into mechanical work, the reservoir with the higher temperature T_1 must also provide a further quantity of heat, which is useless as far as production of work is concerned in that it passes over to a reservoir at the lower temperature T_2 . If the process is reversible, its efficiency is the maximum possible: if it is irreversible, its efficiency is less. The maximum possible efficiency, which is possessed by every reversible engine for the conversion of heat into work, is

$$\eta = \frac{T_1 - T_2}{T_1}.$$

It is therefore dependent only upon the temperatures of the reservoirs and can never be exceeded. A continually working engine of higher efficiency is fundamentally impossible. Such an engine need not be in the slightest degree incompatible with the first law of thermodynamics; but it would necessarily give rise to other processes contrary to all the evidence of experience—evidence which has become so overwhelming that it has been taken as the basis of a second law of thermodynamics. OSTWALD expressed this law in the following form (p. 122).

Perpetual motion of the second kind is impossible.

It is impossible by means of a periodic process to withdraw heat continually from a reservoir and to convert it into work at constant temperature. The presence of a second reservoir at lower temperature, i.e. a temperature difference, is necessary for the conversion of heat into work.

II. As mentioned above, the existence of a heat engine of higher efficiency than the Carnot cycle would also lead to another impossible process. This is the passage of heat from a lower to a higher temperature without the occurrence of any other processes. Hence the second law of thermodynamics may also be expressed in the following form, due to CLAUSIUS (1850):

Heat can never pass spontaneously (i.e. without external influences) from a colder to a hotter body: a temperature difference can never appear spontaneously in a body originally at uniform temperature.

III. The essential meaning, the kernel of the second law of thermodynamics, is contained in the formulation given in 1866 by LUDWIG BOLTZMANN:

Nature tends to pass from a less probable to a more probable condition.

Probability of a Condition.—(See also § 10, section 6, p. 139.) The direction of all spontaneous processes of nature is such as to give rise to a more probable or at least an equally probable condition (pp. 114 and 137). The most probable state for an isolated closed system is that of complete disorder, in which there are no *directed* conditions, such as differences of temperature, of pressure, or of concentration. In this state there is no excess of energy in any one part of the system; the energy distribution is perfectly uniform, and the whole system is therefore at a uniform temperature.

For a further formulation of the second law see immediately below, and also § 10, p. 135.

3. Direction of Natural Processes.—In a closed system all processes take place in such a direction as not to bring the system into a less probable condition. Processes in which the probability remains the same are *reversible*; they can pass through all their phases in the reverse direction. On the other hand, processes causing an increase in the probability of the condition of the system are irreversible.

All purely mechanical and purely electromagnetic processes are reversible and accompanied by no change of probability, provided that dissipation of energy is excluded, i.e. provided that the energy remains in an ordered form (p. 113). The probability of the system also remains constant in reversibly conducted thermal processes. The system must be taken to include all the bodies involved. In Carnot's cycle, for example, the condition of the working substance is in no way changed when the cycle has been completed. The increase of probability which would occur if the passage of the heat from the hotter to the colder heat reservoir took place irreversibly is exactly compensated by the decrease of probability due to the conversion into mechanical work of a part of the heat derived from the hotter reservoir.

Now perfectly reversible processes do not exist in nature. All mechanical and electromagnetic phenomena of matter are associated with an irreversible transformation of ordered into random energy. Hence as a general principle based on experience we may say:

All changes in a closed system occur in the direction in which the sum of all the processes involved is irreversible, i.e. in which the probability of the state of the system is increased.

This is the essence of the second law of thermodynamics.

A closed system is an ideal concept and as such is never actually realized. But the larger a natural system is, the more nearly does it approximate to a closed system. For since all the processes occur within it, the magnitude of the quantities of energy and matter taking part in them will be proportional to the volume of the system, whereas the magnitude of the external influences will be proportional to its surface. Hence the greater the system, the less the relative effect of external influences. On this account, attempts have been made to apply the second law of thermodynamics to the whole universe (see subsection 6 below and p. 135) and to express it in the form:

All natural events occur in such a direction that the universe passes into a more probable state.

In the case of a reversible process both the initial and final states have the same probability; neither of them is preferred above the other. This might be expressed by saying that nature favours both equally. Therefore such a process will not in general occur *spontaneously*. A temperature difference will not equalize itself spontaneously in a reversible manner; nor will a pressure difference in a gas. A liquid will not evaporate reversibly. On the contrary all such processes occurring spontaneously do so in such a way that the system passes into a more probable, more favoured state. Spontaneous processes are therefore irreversible. They can only be *conducted* reversibly (actually approximately reversibly) with the help of special devices. It is also clear from what has been said above that, even if only a small elementary part of a process is irreversible, the final state of the whole system concerned has the greater probability, and the whole system cannot return *spontaneously* into its initial state. Hence in order that a process may be reversible, it must be capable of complete reversal in *all* its elementary parts. A necessary condition for the occurrence of a spontaneous process in a closed system is the presence of a difference of condition within the system. There must be a directed gradient (Vol. I, p. 191) of some property (as of pressure, temperature, concentration, chemical nature, &c.) which urges towards equalization—an order tending to pass into disorder; the system must be provided with the opportunity of passing into a more probable state, i.e. into the maximum possible degree of disorder, by the occurrence of the process.

The physicist often has to deal with cases in which purely mechanical and electromagnetic processes of a reversible nature occur spontaneously. These are processes of oscillation, e.g. the swinging of a pendulum or the discharge of a condenser, which occur without increasing the probability of the system. It must not be forgotten, however, that these processes are usually considered only in their ideal form. Actually processes of oscillation are also accompanied by the development of heat due to friction or electrical resistance and therefore increase the probability of the state of the oscillating system (see also § 10, subsections 3 and 6, pp. 134 and 139).

4. "Order" in Molecular Processes.—It has been thought that processes at variance with the second law of thermodynamics, such as spontaneous appearances of temperature or pressure differences in a gas, might be possible by the inter-

vention of beings (the so-called "demons"*) endowed with intelligence. These might sort out the moving molecules of a gas by operating certain shutter devices, clack-valves or the like. For example, they might separate the more rapidly moving molecules from the more slowly moving ones by allowing only the former to pass through; or with the help of a one-way valve they might collect more molecules in the one part of a space than in the other, thus producing a difference of pressure. The only objection which can be raised to this view is that our experience indicates that such intelligence does not exist in inanimate closed systems in temperature equilibrium. As far as we know, beings endowed with intelligence themselves necessarily require temperature differences and the like; our experience leads us to think that every display of understanding is accompanied by chemical processes. Valves of the type mentioned may possibly play a part in the *living* cell; but as yet we have no indication that this is the case.

5. Limits of Validity of the Second Law of Thermodynamics.—According to **BOLTZMANN'S** formulation, processes at variance with the second law are not impossible, but only in the highest degree improbable. As was shown on p. 114, the probability of any given state of distribution increases as the number of particles involved is made smaller. Hence if the number of particles taking part in the process or the space it occupies is sufficiently small, the probability of the occurrence of the process may become so great that it may actually be observed once within measurable time. The investigation of Brownian molecular movement (p. 54 *et seq.*) has led to the recognition that suspended particles of a size just visible in a microscope possess kinetic energy which they have derived from the thermal energy of their surroundings at uniform temperature, and also that observable variations in the distribution of these particles occur spontaneously in neighbouring small volumes.

The visible motions of the particles are the result of particularly energetic impacts. Thus heat energy has passed over into actual bodies—as distinct from molecules—in a greater degree than that corresponding to thermodynamical equilibrium. (Subsection 6, p. 140.) If we could collect the mechanical (kinetic) energy of these particles, we should be able to obtain mechanical work at the expense of the heat of the surroundings. This would break the second law of thermodynamics. Now all conceivable devices for collecting this kinetic energy prove to be impracticable, because essential parts of them would also show Brownian motion and therefore not function. Imagine, for example, a particle to be constrained to move upon a vertical guide in such a way that it is prevented by a catch from slipping down, but is free to move upwards. Then it would be raised higher and higher by chance impacts of great energy and would thus acquire a store of useful potential energy at the expense of the thermal energy of its surroundings. But the catch would necessarily have to be of the same dimensions as the particle itself or even smaller. Its own irregular Brownian movement would therefore ruin the operation of the mechanism.

We might also dispense with the catch and wait for a chance impact of a particularly favourable character which would raise the particle so high up the guide that we could then make direct use of its potential energy. But a more accurate investigation shows that with increasing thermal energy transmitted to the particles the average lengths of time between successive favourable impacts increase tremendously. (Subsection 6, p. 140.) Hence from a practical point of view such a utilization of heat energy with the help of the Brownian movement is quite impossible. For practical purposes the validity of the second law of thermodynamics is unrestricted.

The particles just considered, their numbers and the volumes concerned, are

* These are often referred to as *Maxwell's demons*, since **MAXWELL** was the first to point out that the second law of thermodynamics might be broken by the intervention of a discriminating intelligence in the course of the processes on the molecular scale.

so small that we cannot speak of a most probable average distribution of particles and thermal energy as we can in the case of larger numbers of particles and greater volumes. Now the statements of the second law of thermodynamics concerning temperature, pressure, concentration, &c., refer to this large-scale average. Regions of the order of magnitude of the particles showing Brownian movement therefore represent the limit down to which the concepts of temperature, pressure, concentration in their usual form still hold, and down to which we can still speak of the general, practical validity of the second law of thermodynamics. Up to the discovery of the phenomena referred to above the second law had been supposed to hold universally for all observable ("macroscopic") processes. It is only in the light of these discoveries that the necessity for and the great significance of Boltzmann's formulation become apparent.

The second law of thermodynamics can therefore make no claim to be universally valid and universally binding.

Amongst very small bodies up to 0.004 mm. in size, we can see processes which do not obey the second law. Amongst larger bodies processes at variance with it are not completely impossible; they are merely so improbable and therefore so rare that they are excluded for practical purposes.

6. Zero-point Energy.—The validity of the second law of thermodynamics is connected with the experimental fact that in all processes a part of the energy concerned is transformed into heat, that is to say into random motion of the molecules. The logical conclusion from this is that all energy must eventually pass into heat and that this heat must distribute itself uniformly throughout the universe. Thus the universe would succumb to a "thermal death". Admitting the correctness of this unjustifiable extension of these principles beyond the realm of our experience, this state could only be attained provided that the amount of matter is conserved, i.e. provided that the number of molecules sharing the heat motion is constant. We know to-day, however, that the atoms making up the molecules may break down under certain conditions (radioactivity, nuclear rupture, see Vol. V), thereby setting free extremely large quantities of energy at certain points. Thus as a result of this internal atomic energy (which is still present even at the absolute zero of temperature—*zero-point energy*—and which, as far as we know, is independent of the temperature) differences of energy and temperature are always being produced and physical processes thereby made possible. But these atomic changes can only postpone "thermal death", not prevent it; for observations so far carried out indicate that radioactivity is a disintegration of matter, so that in this respect also there must eventually be a state of uniformity, of death. Our present knowledge of the structure of matter (Vol. V) is in no way incompatible with the idea that conditions may exist in the universe under which radioactive matter is spontaneously formed again (NERNST). This would provide a process continually supplying new energy differences from the disintegration of matter, and therefore new "life" to the chain of physical events. Hence it is possible that the second law of thermodynamics has limits in that statistical fluctuations (of the kind that always occur on the molecular scale, e.g. very small regions of "high temperature" or of "high pressure") may under special conditions attain a certain *permanence*, for example as a result of the formation of radioactive molecules whose stability is almost infinitely great in comparison with thermal fluctuations. In this way these fluctuations would as it were be retarded to an enormous extent and would thus come into the order of magnitude apprehensible by us human beings. Hence, just as the existence of Brownian movements would exclude the possibility of a "thermal

death" of the universe for beings of molecular dimensions, so also would such a "death" of the universe be impossible in our case if the above formation of radioactive matter actually occurred. Instead of succumbing to a "thermal death", the universe would "live" eternally in the ebb and flow and endless rhythm of physical change.

10. Entropy

1. **Reduced Quantity of Heat.**—So far we have been concerned chiefly with that part of the quantity Q_1 of heat which can be converted into mechanical work. We will now make use of the equation

$$Q_1 - Q_2 = \frac{T_1 - T_2}{T_1} Q_1$$

(already mentioned several times above) to derive a relationship between the quantity Q_1 of heat absorbed and the quantity Q_2 given out again by the gas in Carnot's cycle.

From p. 120 we have

$$\frac{Q_2}{T_2} = \frac{Q_1}{T_1}.$$

If, as on p. 119, we take quantities of heat supplied as positive and quantities withdrawn as negative, we must write this equation in the form

$$\frac{-Q_2}{T_2} = \frac{Q_1}{T_1}, \quad \text{or} \quad \frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0.$$

Following the nomenclature of H. A. LORENTZ,* the quotient of a quantity of heat by the temperature at which it is absorbed or given out by a process may be called a **reduced quantity of heat**. The last equation can then be expressed as follows:

In a Carnot cycle the sum of the reduced quantities of heat supplied to and withdrawn from the working gas is equal to zero.

Any reversible cyclic process can be divided up into a large number of elementary Carnot cycles (see fig. 17, p. 123), such that the final temperatures of certain of them coincide with the initial temperatures of certain others. This last condition is inessential for the present considerations; all that we need notice is that the temperatures at which heat is supplied and withdrawn respectively are different in different elementary cycles. Hence the elementary quantities of heat must be reduced in every case to the proper temperature at which they are absorbed or given out in the corresponding elementary Carnot cycle. If the whole cyclic process is to be a continuous succession of elementary Carnot cycles, the quantities of heat supplied or withdrawn in the successive elements must be infinitesimally small. Consider any one of these elements, e.g. that shaded in fig. 17, p. 123. Let the quantity of heat ΔQ_m be absorbed at the initial temperature T_m and the quantity $-\Delta Q_n$ given out again at the final temperature T_n .

* H. A. LORENTZ (1853–1928), Professor of Theoretical Physics at Leiden, one of the leading theoretical physicists of the last generation. He received the NOBEL prize in 1913.

Then the sum of the reduced quantities of heat involved in this elementary Carnot cycle must be zero, i.e. we must have the equation

$$\frac{\Delta Q_m}{T_m} + \frac{\Delta Q_n}{T_n} = 0.$$

Corresponding equations also hold for every one of the elementary cycles. Adding all of them together we have

$$\sum \frac{\Delta Q}{T} = 0.$$

In the limit when all the temperature steps become infinitesimally small, this sum becomes an integral and we obtain the important equation

$$\oint \frac{dQ}{T} = 0.$$

The circle through the integral sign indicates that the integration is to be extended over the whole cyclic process, i.e. round the whole of the periphery of the closed figure in fig. 17, p. 123.

In this equation all quantities of heat supplied are to be reckoned as positive and all quantities of heat withdrawn as negative. Each elementary quantity is then to be divided by the absolute temperature at which it is supplied or withdrawn. The equation can be expressed in words as follows:

In every reversible cyclic process the algebraic sum of the reduced quantities of heat supplied and withdrawn is equal to zero.

2. Entropy.—Imagine a body, whose state is represented by the point A in fig. 19, to pass over into the state E by means of a reversible process (not a cyclic process). Then:

The sum of the reduced quantities of heat supplied or withdrawn during a given reversible process is independent of the path along which the process takes place.

In order to prove this theorem, imagine the process to take place along the path AHE and a closed reversible cycle to be completed by the performance of the reverse process along the different path EZA. If the sum of the reduced quantities of heat necessary for the process AHE is X and the corresponding sum for the process EZA is Y, then we must have $X + Y = 0$.

Suppose now that the sum of the reduced quantities of heat required for the process along some other path AH₁E is X₁. We can also combine this path with the reverse path EZA so as to make a closed reversible cyclic process. Hence also $X_1 + Y = 0$. From the two equations it follows that $X = X_1$.

The value of the integral

$$\int_A^{(rev.)} \frac{dQ}{T}$$

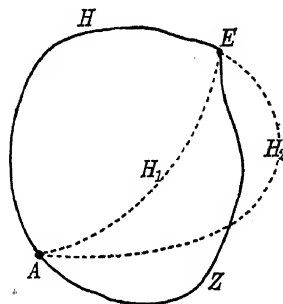


Fig. 19

which gives the sum of the reduced quantities of heat supplied or withdrawn during the reversible change from the state A to the state E, is therefore independent of the path, i.e. independent of the nature of the process. Its value depends only upon the initial and final states. Hence for each state of the body there exists a quantity S , which has the value S_A in the state A and the value S_E in the state E, and which is such that the difference $S_E - S_A$ is equal to the sum of the reduced quantities of heat involved when the change takes place along any reversible path. Hence the elementary reduced quantity dQ/T of heat involved in the passage of the body from one state to another infinitesimally different from it is equal to the element dS of the quantity S ; expressed in mathematical terms, it is equal to the *complete differential* dS of the characteristic quantity S .

The difference $S_E - S_A$ is called the **entropy** (dimensions: [erg.deg.⁻¹]) of the body in the state E relative to the state A.

The **absolute value** of entropy cannot be obtained directly. Hence it is necessary to fix an arbitrary reference or zero state to which all other states can be referred. In other words, the entropy of a body involves an arbitrary additive constant, namely, the entropy of the body in the reference state. Putting this constant equal to S_0 , the entropy S of any other state is given by the equation

$$S - S_0 = \int_{\text{rev.}} \frac{dQ}{T},$$

in which the integral is to be extended over the path along which the body passes *reversibly* from the reference state into the state under consideration. The entropy S has the same value for all reversible paths. It is therefore defined for all states into which the body can be brought reversibly. Now experience teaches that there is no state into which a body cannot be brought in a reversible manner. *Hence the entropy of a body is defined for all states except in so far as it involves the same additive constant in each case.* If the passage from the state 1 to the state 2 is reversible then

$$S_2 - S_1 = \int_1^2 \frac{dQ}{T} \quad (\text{rev.})$$

The entropy of a body is proportional to its mass. Hence entropy is referred to unit mass. The entropy of a system of bodies is equal to the sum of the entropies of the individual constituents.

3. Entropy in the Case of Irreversible Processes.—Consider first the case in which a body performs a reversible cyclic process. It is supplied with heat from the sources 1, a part of which it gives up again to the receivers 2 at lower temperature, the rest being converted into work of some kind. Since the body performs a cycle, it must return to its

original condition, i.e. to its original entropy. Hence $S_1 = S_2$ and for any reversible cyclic process

$$\oint_{(\text{rev.})} \frac{dQ}{T} = 0.$$

The integral is to be extended over all the elementary quantities of heat supplied to or withdrawn from the body, the former being reckoned as positive and the latter as negative. *T is the temperature of the body at which the corresponding elementary quantity of heat is absorbed or given out.* Since the process is reversible, *T* is identical at every instant with the temperature of the heat reservoir with which the working body is in thermal contact.

When the cyclic process occurs irreversibly, the integral assumes a value different from zero; but in general it is not possible to state the nature of this difference. *If T is put equal to the temperature of the heat reservoir*, which in irreversible processes may differ by a finite amount from the temperature of the body, experience shows that the integral assumes a negative value, i.e. that

$$\oint_{(\text{irr.})} \frac{dQ}{T} < 0.$$

A few examples may be given by way of illustration.

I. Consider first the case in which friction reduces the efficiency of the conversion of heat into work below the value corresponding to frictionless (i.e. reversible) working. Let the quantity of heat supplied to the body (e.g. a gas engine) from the heat reservoir 1 be Q_1 . Then a smaller fraction of Q_1 will be converted into useful work and a larger fraction given up to the colder reservoir than would be the case if there were no friction. The negative part of the integral is therefore increased. On the other hand, if the frictional heat is returned to the hotter source, the positive part of the integral is diminished. Thus in both cases the integral assumes a negative value.

II. The equalizations of temperature between the body and the heat reservoirs may occur with finite speed, because the temperature of the body is lower by a finite amount than that of the hotter reservoir or greater by a finite amount than that of the colder reservoir. Now *T* is put equal to the temperature of the reservoir instead of the body. In the first case (positive dQ) the value used in the integral will therefore be too high; and in the latter case (negative dQ) too low. Thus the positive part of the integral will be reduced and the negative part increased in comparison with the case of reversible action. Hence the value of the integral is again negative.

III. Irreversible action may also be due to finite differences between the external pressure and the pressure of the working substance (e.g. the pressure in the cylinder of a gas engine). The work performed during expansion is then less than in the reversible case of continuous pressure equilibrium. Hence less heat is absorbed from the heat source for conversion into work; consequently the positive parts of the integral are diminished. Conversely an excess of external pressure during compression causes the performance of too great an amount of work upon the body. An equivalent quantity of heat is given up to the colder reservoir and the negative parts of the integral are increased.

Thus all the above factors rendering the process irreversible cause the integral to assume a negative value. The general conclusion is that the value of the integral is negative for any irreversible cyclic process, i.e.

$$\oint_{(\text{irr.})} \frac{dQ}{T} < 0.$$

It is now a simple matter to derive a general theorem as to the relation between the entropy and the value of the integral for an irreversible process by which the body passes from the state 1 to the state 2. For if we bring the body back from the state 2 into the state 1 again by a reversible process, then for the whole irreversible cycle we have

$$\int_1^2 \frac{dQ}{T}^{(\text{irr.})} + \int_2^1 \frac{dQ}{T}^{(\text{rev.})} < 0.$$

But the latter integral is equal to the difference $S_1 - S_2$ of the entropies of the body in the two states. Hence

$$\int_1^2 \frac{dQ}{T}^{(\text{irr.})} + S_1 - S_2 < 0$$

or

$$S_2 - S_1 > \int_1^2 \frac{dQ}{T}^{(\text{irr.})}$$

In the case of an irreversible process the difference of the entropies of the body in the initial and final states is greater than the integral $\int_1^2 dQ/T$.

From this follows an important theorem for *closed systems*, i.e. for systems completely isolated from their surroundings. In this case dQ is always equal to zero. The integral therefore vanishes and we have

$$S_2 - S_1 > 0.$$

That is to say:

The direction of irreversible processes within a closed system is always such that the entropy of the system increases.

In the limiting case of reversibility the sign of inequality is replaced by that of equality: the entropy of the system remains constant. The case never occurs in which the entropy of a closed system is diminished by any process of any kind.

If the entropy is to diminish, the system cannot be a closed one, but must be subject to external influences. If the system be enlarged so as to take in the sources of these influences, the whole is once more closed. The total entropy obtained by the addition of the entropies of all the bodies involved in a process must increase, or in the limit

remain constant. This limiting case is never actually realized, because all real processes are strictly speaking irreversible.

On this account the following generalization has been made:

On the whole all processes take place in such a way that the entropy of the universe always increases.

This is a further formulation of the second law of thermodynamics; but it exceeds the bounds of our experience. It is still an unsolved and debatable question whether we are justified in applying to the energy forms of *life* all the conclusions drawn from the relationships between the energy forms in *inanimate* processes. It is conceivable that in the living cell there may be valves or membranes permeable in one direction only, such as might produce decreases of entropy. In the light of modern knowledge the existence of processes causing a decrease of entropy has also become quite thinkable (see p. 128).

The first law of thermodynamics determines the quantitative equivalence between thermal and mechanical energy *without reference to the question whether the transformation of the one into the other can actually take place*. The second law, on the other hand, determines the *direction* in which such a transformation can occur.

4. Practical Application of the Concept of Entropy.—We cannot in this book go into all the extremely numerous applications of the two laws and of the concept of entropy in scientific and technical thermodynamics. For these the reader should consult a special work. We will merely illustrate by one simple example the fact that an equalization process is accompanied by an increase of entropy.

Consider the process of temperature equalization involved in the mixing of two equal quantities of water each of 1 kg. mass, the one at the temperature T_1 and the other at the temperature T_2 . Letting the entropy in an arbitrary reference state of temperature T_0 be S_0 , we can calculate the entropies of the two masses of water before mixing relative to this reference state. We have

$$dQ = mc dT,$$

where m is the mass and c the specific heat. In our case $m = 1$ and $c = 1$ and therefore

$$dQ = dT.$$

Making use of this we have for the first mass

$$S_1 - S_0 = \int_{T_0}^{T_1} \frac{dQ}{T} = \int_{T_0}^{T_1} \frac{dT}{T} = \log_e \frac{T_1}{T_0}.$$

Similarly for the second mass

$$S_2 - S_0 = \log_e \frac{T_2}{T_0}.$$

The sum of the entropies relative to the reference state before mixture is therefore

$$S' = S_1 + S_2 - 2S_0 = \log_e \left(\frac{T_1 T_2}{T_0^2} \right).$$

After mixture and equalization of temperature the total mass of 2 kg. has the temperature $\frac{1}{2}(T_1 + T_2)$. Its entropy is therefore

$$S'' = 2(S_m - S_0) = 2 \log_e \left(\frac{T_1 + T_2}{2T_0} \right) = \log_e \left(\frac{T_1 + T_2}{2T_0} \right)^2.$$

As a result of mixing the total entropy has altered by the amount $S'' - S'$, given by

$$\begin{aligned} S'' - S' &= \log_e \left(\frac{T_1 + T_2}{2T_0} \right)^2 - \log_e \frac{T_1 T_2}{T_0^2} = \log_e \left[\frac{(T_1 + T_2)^2}{4T_0^2} \cdot \frac{T_0^2}{T_1 T_2} \right] \\ &= \log_e \left[\frac{(T_1 + T_2)^2}{4T_1 T_2} \right]. \end{aligned}$$

But $(T_1 + T_2)^2 = 4T_1 T_2 + (T_1 - T_2)^2$,

i.e. $\frac{(T_1 + T_2)^2}{4T_1 T_2} = 1 + \frac{(T_1 - T_2)^2}{4T_1 T_2}$.

Therefore $S'' - S' = \log_e \left[1 + \frac{(T_1 - T_2)^2}{4T_1 T_2} \right]$.

Since now the second term in the bracket is certainly positive, the whole expression in the bracket must be greater than unity and therefore the right-hand side of the equation certainly greater than zero. Hence

$$S'' > S'.$$

A similar calculation can be performed for every equalization process. *In all such cases there is an increase of entropy*, because the whole system concerned performs an irreversible process.

A knowledge of the entropy of a body is of great importance for technical purposes, because it determines the *work value* of the body for thermal processes. The entropies of technically important substances (e.g. steam) have therefore been determined empirically. It is only possible to calculate entropy values if the equation of state be known. But for vapours or even for real gases this deviates considerably from that of a perfect gas. In the case of a perfect gas we have

$$dQ = dU + p dV = c_v dT + p dV.$$

Hence the entropy S per unit mass is given by

$$\begin{aligned} S &= \int \frac{dQ}{T} = \int \frac{1}{T} (c_v dT + p dV) = \int c_v \frac{dT}{T} + \int \frac{p}{T} dV \\ &= \int c_v \frac{dT}{T} + \int \frac{R}{M} \frac{dV}{V} = c_v \log_e T + \frac{R}{M} \log_e V + \text{const.}, \end{aligned}$$

where M is the molecular weight. For an adiabatic change we have

$$dQ = 0.$$

and therefore

$$S = \text{const.}$$

Hence the entropy remains constant during adiabatic processes.

The technical significance of entropy may be illustrated by the following example:

A quantity $Q_1 = 1000$ kcal. of heat, which may be imagined for simplicity to be stored up in liquid water at temperature T_1 , represents an energy of 427,000 m. kg. Only a part of it can be converted into a useful form, however. The remainder

$$Q_2 = \frac{Q_1}{T_1} T_2,$$

where T_2 is the final temperature of the heat engine employed, is useless and is necessarily lost during the conversion of the other part into work. We see that the quotient Q_1/T_1 , i.e. the entropy in the state 1, is of considerable importance for this loss. The final temperature T_2 of the heat engine will generally be room temperature or somewhat higher. We will take it as 30°C . We will further suppose that the 1000 kcal. of heat are stored up in liquid water at 130°C . Actually this will require about 10 litres of water, which will naturally have to be under a correspondingly high pressure. In this case only the fraction

$$\frac{T_1 - T_2}{T_1} = \frac{100}{403},$$

or about 25 per cent of the total heat energy (about 106,000 m. kg.) is obtainable as mechanical work even under the most favourable conditions. If the initial temperature of the water (in this case about 5 litres) is $T_1 = 230^\circ \text{C}$., then the fraction $200/503$ or about 40 per cent of the heat (about 170,000 m. kg.) is utilizable. This shows clearly the great advantage of making the initial temperature as high as possible. The endeavours of engineering are therefore directed towards this end (see § 16, p. 153 *et seq.*).

5. Entropy and Probability.—It has been shown above that all processes in a closed system take place in such a way that both the entropy and the probability of the state of the system increase. Entropy and probability are therefore presumably closely related to one another. This relationship can in fact be expressed in mathematical form.

Consider a system consisting of two bodies in thermal connexion. The body 1 possesses the quantity Q_1 of heat, the body 2 the quantity Q_2 . The probabilities of these states are functions of the respective quantities Q_1 and Q_2 , i.e.

$$P_1 = f_1(Q_1) \quad \text{and} \quad P_2 = f_2(Q_2).$$

Here P_1 is the probability that the body 1 will possess the energy Q_1 and P_2 the probability that the body 2 will possess the energy Q_2 . Then according to the theory of probability, the probability P that the body 1 will possess the energy Q_1 , and *simultaneously* the body 2 the energy Q_2 is given by the product of the separate probabilities, i.e.

$$P = P_1 P_2.$$

This is the probability of the system composed of the two bodies in this state. It must therefore tend towards a maximum value. Now the condition for a maximum is

$$dP = 0,$$

$$\text{i.e.} \quad dP = d(P_1 P_2) = P_1 dP_2 + P_2 dP_1 = 0,$$

$$\text{or} \quad \frac{dP_1}{P_1} + \frac{dP_2}{P_2} = 0.$$

Since no other bodies are involved and the two bodies 1 and 2 form a closed system, we must also have

$$dQ_1 + dQ_2 = 0.$$

Combining the last two equations, we obtain the condition for the statistical equilibrium towards which the system tends, viz.:

$$\frac{1}{P_1} \frac{dP_1}{dQ_1} = \frac{1}{P_2} \frac{dP_2}{dQ_2}.$$

But we know from experience that this equilibrium is attained when the two bodies are at the same temperature, i.e. when $T_1 = T_2$.

We may therefore regard the quantity

$$\frac{1}{P} \frac{dP}{dQ} = \frac{d(\log_e P)}{dQ}$$

as a measure of temperature. Setting it inversely proportional to the temperature, we obtain

$$k \frac{d(\log_e P)}{dQ} = \frac{1}{T}$$

where k is a constant.

A comparison of this with the equation expressing the thermodynamical definition of entropy,

$$\frac{dS}{dQ} = \frac{1}{T},$$

gives the relationship between entropy and probability.

In this way we obtain the equation

$$S = k \log_e P + \text{const.}$$

Since the entropy itself involves an arbitrary additive constant, we may omit the constant of integration. The value of the constant k (the **BOLTZMANN** entropy constant) can be obtained by methods which cannot be discussed here. It comes out to $\frac{2}{3}L$ (for the definition of L see p. 38), which is the same as the value found on p. 41 for the energy of a linear oscillator at a temperature of 1° abs. (For further details see Vol. V—Heat Radiation.) The numerical value of k is $1.37 \cdot 10^{-16}$ ergs/degree.

The last equation gives an essentially *new definition of the entropy* of a system.

The entropy of a state is a definite multiple of the natural logarithm of its probability.

The concept of entropy, which is very difficult to grasp from the purely thermodynamical point of view, becomes easier to understand in the light of this definition. The general and precise determination of the magnitude of entropy is one of the most important problems of the statistical method of treatment. In the first place a more exact definition must be given of what is to be understood by the probability of a state. A detailed discussion of this lies naturally outside the scope of this book, but the following brief indications may be given.

In a gas, which is to be regarded as composed of an immense number of individual molecules, any given instantaneous state is only mechanically determined provided that we know the corresponding position and velocity of every molecule. This knowledge is not necessary, however, for the macroscopic treatment of processes in which the elementary particles are moving at random. For this purpose it suffices to know how many of the particles lie within any given space or velocity interval. Thus the macroscopic state is determined by the space and velocity *distribution*. Now it is obvious that each such distribution is realizable

in many different ways, because it can be formed by many different groupings of the individual particles (in the case of a gas, the molecules). Consider the case, for example, in which 4 out of 10 similar balls are in a compartment A and the remaining 6 in another compartment B connected to it. This state is realizable in a large number of ways. Imagine the balls to be marked with the numbers 1 to 10. Then in A we may have the balls 1, 2, 3 and 4 or 1, 2, 3 and 5 or 1, 2, 3 and 6, &c.; or 2, 3, 4 and 5 or 2, 3, 4 and 6, &c., and so on. The state of 4 balls in A and 6 in B is therefore realizable by a large number of so-called *complexions*. Each of these complexions is exactly equivalent to each of the others as far as the realization of the state is concerned, though considered more closely they are all different. In the complete molecular disorder of a gas the state is, as it were, completely independent of what mark any particular molecule bears, being characterized only by the possible number of complexions. This number is called the *probability of the state*. The larger it is, the more the state will predominate over other possible states. The calculation of the number of complexions of a given state is a statistical problem and may be solved according to the rules of the theory of probability.

6. Rarity of Transitions into an Ordered State.—In the light of the concept of probability the results of thermodynamics lose their character of absolutely binding laws; they are shown rather to be mere rules, true in the majority of cases but liable to be broken in exceptional circumstances. It is therefore instructive to see by means of a numerical example to what extent this can invalidate the purely thermodynamical conclusions as to the occurrence of a process.

Consider two bodies at the respective temperatures $T_1 = 273 + 27 = 300^\circ$ abs. and $T_2 = 273 + 28 = 301^\circ$ abs. Let the conditions be such that normally a quantity of heat energy equivalent to 1 erg passes over from the hotter to the colder body in a certain interval of time. We will first investigate the amount by which the probability W_2 of the final state differs from that W_1 of the original state. The entropy change ΔS is given by

$$\Delta S = \frac{1}{300} - \frac{1}{301} = \frac{1}{9} \cdot 10^{-4} \text{ erg/degree.}$$

From the entropy-probability equation on p. 138 we have

$$\Delta S = \frac{1}{9} \cdot 10^{-4} = k \log_e \frac{W_2}{W_1},$$

$$\text{or} \quad W_2 = W_1 e^{\frac{\Delta S}{k}} = W_1 e^{\frac{10^{-4}}{9 \cdot 1 \cdot 37 \cdot 10^{-16}}} = W_1 e^{\frac{10^{12}}{12}} = W_1 e^{\frac{100}{12} \cdot 10^{10}}$$

$$\text{Therefore} \quad \frac{W_2}{W_1} > 1000^{10^{10}}.$$

Thus the probability of the final state is an enormous number of times greater than that of the initial state. Here W_1 is the number of complexions of equal probability by means of which the initial state can be realized. Similarly W_2 is the number of complexions of the final state. According to the present method of treatment each one of these $W_1 + W_2$ independent complexions is of exactly equal probability. The fact that the second state is the more probable is due solely to its very much greater number W_2 of complexions. Of the $W_1 + W_2$ possible complexions, W_2 correspond to the passage of heat from the hotter to the colder body, W_1 to the absence of such a process. In accordance with the theory of probability, the probability W that the process will be observed in a given time is given by the quotient of the number of favourable cases divided by the total number of possible cases, i.e.

$$W = \frac{W_2}{W_2 + W_1} = \left(1 + \frac{W_1}{W_2}\right)^{-1}.$$

Since the term W_1/W_2 is very small, we may write

$$W = 1 - \frac{W_1}{W_2}.$$

Similarly the probability W' that heat will not pass from the hotter to the colder body is

$$W' = \frac{W_1}{W_2 + W_1},$$

for which we may write approximately

$$W' = \frac{W_1}{W_2} = 1 : 1000^{10^{10}}.$$

This means that on an average the thermodynamically required transition of heat from the hotter to the colder body would be found not to occur in at most one out of $1000^{10^{10}}$ observations carried out under the same conditions. Now $1000^{10^{10}} = 1000^{10,000,000,000}$ is an unimaginably large number. If every digit took up a space of 4 mm. the strip of paper required to write out $10^{10^{10}}$ would be $4 \cdot 10,000,000,000$ mm. = 40,000 km. long, i.e. long enough to go once round the earth. The number $1000^{10^{10}}$ would require a strip three times as long. Hence there is only an unimaginably small probability that, in many thousands of years—at least in periods covering the whole of human history—and amongst all the observers of the world, one case will arise in contradiction to the requirements of thermodynamics. For practical purposes, therefore, the probability of thermodynamically required processes amounts to complete certainty.

We arrive at a different result if we consider a very much smaller quantity of heat than 1 erg, for example, $12 \cdot 10^{-12}$ erg. Then by a similar calculation we obtain

$$\frac{W_2}{W_1} = e = 2.7,$$

whence

$$W = \frac{W_2}{W_2 + W_1} = \frac{2.7}{3.7} \quad \text{and} \quad W' = \frac{W_1}{W_2 + W_1} = \frac{1}{3.7}.$$

In this case the small quantity of heat considered would be found on the average to have passed over from the hotter to the colder body in only 27 cases out of every 37. In the other 10 cases it would be found not to have passed over, and would thus have contradicted the requirements of thermodynamics. From this we conclude that the larger the amount of energy involved, the rarer and more improbable are exceptions from the normal course of thermodynamical processes. Even the passage of a quantity of thermal energy equivalent to 1 erg—a very small quantity compared with those involved in our usual measurements—from a hotter to a colder body takes place practically without exception. But in the case of very small amounts of energy, such as those involved in molecular changes, processes at variance with the rules of thermodynamics may very well be encountered (§ 9, p. 129).

7. Statistical Fluctuations.—Owing to the random nature of molecular motion it follows that excesses of very rapidly moving molecules (a high “temperature”) or of very slowly moving molecules (a low “temperature”) may occur in very small volume elements and for very short times. In the same way the “pressure” in very small

volume elements is continually fluctuating. Under certain circumstances these fluctuations may become visible; for instance in the Brownian movement, where the density of distribution and the velocity of motion of the particles can be seen to vary under the microscope. Similar phenomena can also be observed in the vaporization of liquids near the critical point. At constant critical pressure the volume of the gas just above the critical temperature is very much greater than that of the liquid just below. Hence a very slight change of temperature causes a very great change of volume. The statistical fluctuations of the thermal motion must be accompanied by very great fluctuations of density. Consequently very small liquid regions are continually being formed in a gas which is kept at constant critical pressure and temperature—tiny liquid droplets which disappear again at once and reappear suddenly at other points. On account of this marked lack of uniformity the gas appears opalescent in this state (*critical opalescence*). The measurement of this opalescence provides a method of determining the Loschmidt number. A determination of this sort has actually been carried out successfully (KAMERLINGH-ONNES) in the case of ethylene.

11. Combination of the First and Second Laws of Thermodynamics

In the course of the above treatment we have had to deal with certain quantities which are descriptive of the state of a given system in that they have a definite numerical magnitude for every state. These quantities are: internal energy U , pressure p , volume V , temperature T , concentration as given by the number N of dissolved molecules, and finally the entropy S . They are not independent of one another but are connected by certain functional relationships determined by the nature of the system. A change of one of these *parameters of state** causes in general a change of the others, although one or more of them may remain constant.

For example, when a perfect gas alters its volume without performing external work or having external work done upon it, its internal energy and temperature remain constant. The process is thus an isothermal one at constant internal energy. The internal energy of a perfect gas depends only upon the temperature and therefore remains constant as long as the temperature remains constant. The state of the system can be varied while one of the parameters is kept constant: e.g. isopiestic† processes ($p = \text{const.}$), isochoric‡ processes ($v = \text{const.}$), isothermal processes ($T = \text{const.}$), isentropic processes ($S = \text{const.}$), processes at constant concentration, and so on. During an (infinitesimal) change the system will in general receive from or give up to the surroundings a quantity dA of work and a quantity dQ of heat. But here again the condition may be imposed that there shall be no external work done by or upon the system ($dA = 0$) or that there shall be no gain or loss of heat ($dQ = 0$.) The latter type of process is the *adiabatic*

* Gr., *parametrein*, to measure. † Gr. *piézēin*, to compress. ‡ Gr., *chōrema*, volume.

type. If simultaneously $dA = 0$ and $dQ = 0$, then the system is a closed one, because it cannot gain or lose energy of any kind.

The equation for the first law of thermodynamics is

$$JdQ = dU + dA,$$

where dQ is the quantity of heat supplied to the system, dU the increase of internal energy and dA the external work performed by the system. In the case of *reversible* processes we may introduce the entropy S , thus combining the first and second laws by means of the equation

$$JTdS = dU + dA.$$

For adiabatic processes $dQ = 0$; the external work is performed at the expense of the internal energy of the system, i.e. in the case of a perfect gas there is a corresponding fall in temperature. A reversible adiabatic process is at the same time isentropic.

Internal Energy.—When none or only a part of the heat supplied to the system is used up for the performance of external work, i.e. when $dA = 0$ or $< JdQ$, the internal energy must increase.

The nature of this change of internal energy leads to theories of the constitution of matter identical with those which form the basis of the kinetic theory of gases (§ 1, p. 35 *et seq.*). Thus in the simplest type of substance, a monatomic gas, the heat supplied causes an equivalent increase of the kinetic energy of molecular translation. This appears as a rise of temperature of the gas and, at constant volume, as a rise of pressure. In the case of a diatomic gas the heat added is partly used up in increasing the kinetic energy of translation of the molecules, i.e. in raising the temperature and, at constant volume, also the pressure; but a part goes to strengthen internal motions (atomic vibrations) within the molecules, i.e. to increase the amplitude of the intramolecular vibrations and their periodic energy transformations (kinetic into potential and vice versa). This latter part of the heat energy supplied does not cause any rise of temperature. The internal energy is very complicated in the case of solids and liquids, because in addition to the complex structure of the molecules there are also combinations of the molecules with one another to be taken into account (forces of cohesion).

External Work.—Unless some special constraint is applied, changes of the temperature of a body are in general accompanied by changes of length or volume. If the body is subjected to external forces, these changes perform work. For instance, in the case of a rod expanding and raising a weight the quantity of work performed is given by the product of the weight into the height through which it is moved. An increase dV of volume against a pressure p performs the *external work* $p dV$ (p. 33). In the case of solids and liquids this can be neglected in comparison with the *internal work*. In the case of gases, however, the external work is the main part—for a perfect gas the whole—of the work performed. The equation of the first law of thermodynamics for systems where $p dV$ is the only external work performed is

$$JdQ = dU + p dV.$$

For reversible processes combination with the second law gives

$$JT dS = dU + p dV.$$

Experience shows that the two laws can also be extended to systems in which other kinds of external work are performed, such as elastic deformations, chemical changes, solution, electrical work, and the like. In all such cases the work done can be measured by the product of a generalized force parameter P and the change dV of another parameter. Examples: electrical work = electromotive force \times quantity of electricity; work against surface tension = surface tension \times change of surface area; chemical work = chemical force \times amount transformed; work of solution = solution pressure \times amount dissolved; elastic work = stress \times change of strain; and so on. For a system capable of performing any of these types of work we have

$$J dQ = JT dS_{(\text{rev.})} = dU + \Sigma P dV.$$

The Clausius-Clapeyron Equation.—This is an important relation connecting the latent heat of a vapour, the change of volume due to evaporation, and the rate at which the saturation pressure changes with the temperature. The relation is readily obtained as follows.

Consider a Carnot cycle in which the working substance consists of a liquid with its vapour. Throughout the operations the two phases are supposed to remain in equilibrium with each other, or, in other words, the vapour always remains saturated while the temperature and pressure change. This gives a Clapeyron diagram (p. 117) in which the isothermals are lines of constant pressure and therefore horizontal, and these are connected by two adiabatic curves.

As on p. 117, let T_1 and T_2 be the two temperatures considered, and let p_1 and p_2 be the corresponding saturation pressures. Also, let L_1 be the latent heat of unit mass at temperature T_1 .

In the first operation, we suppose unit mass of the liquid, at temperature T_1 , to be changed into vapour at the same temperature and at pressure p_1 . The heat supplied is therefore L_1 .

The efficiency is
$$\frac{T_1 - T_2}{T_1}.$$

The work done is therefore
$$JL_1 \frac{T_1 - T_2}{T_1}.$$

But the work done is equal to the area of the Clapeyron diagram. To obtain a simple expression for this area we shall suppose the change of temperature $T_1 - T_2$, and therefore also the change of pressure $p_1 - p_2$, to be very small.

Let V_l be the volume of unit mass of the liquid, and V_v that of unit mass of the vapour.

The change of volume in the first operation is $V_v - V_l$. The diagram is practically a parallelogram with base $V_v - V_l$ and height $p_1 - p_2$; its area is therefore $(V_v - V_l)(p_1 - p_2)$.

Thus we find

$$(V_v - V_l)(p_1 - p_2) = JL_1 \frac{T_1 - T_2}{T_1},$$

or
$$V_v - V_l = \frac{JL_1}{T_1} \frac{T_1 - T_2}{p_1 - p_2}.$$

Now let $T_1 - T_2$ and $p_1 - p_2$ become indefinitely small, and write T, L instead of T_1, L_1 . We obtain the exact equation

$$V_v - V_l = \frac{JL}{T} \frac{dT}{dp},$$

or, as it may also be written,

$$\frac{dp}{dt} = \frac{JL}{T(V_v - V_l)}.$$

This is the famous Clausius-Clapeyron equation, giving the change of vapour pressure with temperature. A similar equation applies also to the melting of solids, the proof for this case being practically identical with the above.

Example.—Find how much the boiling-point of water is lowered when the atmospheric pressure falls from 760 mm. to 750 mm. of mercury.

Here $L = 539 \text{ cal./gm.}$
 $V_v = 1674 \text{ c.c./gm.}$
 $V_l = 1 \text{ c.c./gm.}$
 $J = 4.2 \times 10^7 \text{ ergs/cal.}$
 $T = 373^\circ \text{ C. abs.}$

The equation gives
$$\frac{dp}{dt} = \frac{4.2 \times 10^7 \times 539}{373 \times 1673}$$

$$= 3.627 \times 10^4 \text{ dynes per sq. cm. per degree C.,}$$

which, on multiplication by $760/(1.013 \times 10^6)$, gives

$$\frac{dp}{dt} = 27.2 \text{ mm. of mercury per degree C., at } 100^\circ \text{ C.}$$

Hence, for a fall of pressure from 760 to 750 mm., the boiling-point falls by $10/27.2$ degrees, i.e. by 0.37° C.

12. Thermochemical Relationships

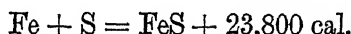
Almost all chemical processes are accompanied by change of temperature. In most cases there is a rise of temperature; heat is developed during the process, which is then said to be **exothermic**.*

* Gr., έξω, outside.

Exothermic processes usually continue of themselves when once they have been started. As examples we may mention the burning of a candle, the combination of hydrogen and chlorine to hydrogen chloride, the explosion of gunpowder, &c. Other processes only take place provided that heat is continually supplied (analogously to the evaporation of water); they use up this heat without rise of temperature. If they occur without heat being supplied, the temperature of the bodies taking part is lowered (**endothermic * processes**).

The quantity of heat set free or absorbed during a given chemical process is proportional to the mass of the substances taking part in it.

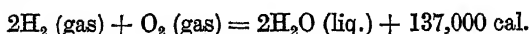
Heat of Combination.—The quantity of heat used up or developed in a chemical combination is known as the *heat of combination*. It is reckoned as negative in endothermic processes and positive in exothermic ones. Since the symbols for the elements in chemical equations also stand for gramme-atoms, heats of combination are also referred to the same units. Thus we write, for example,



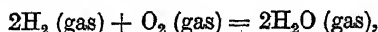
This means that 23,800 cal. of heat are set free when 56 gm. of iron and 32 gm. of sulphur combine to form 88 gm. of ferrous sulphide (a reaction which takes place spontaneously when the elements are intimately mixed, the mixture becoming white hot).

In these processes account must also be taken of any mechanical work which may be performed in addition to the generation of heat. This work is generally that done against atmospheric pressure by the change of volume accompanying the process and must be added in with the heat of combination (positive or negative). In cases where doubt is possible it is therefore necessary to specify in the equation the state of the substances involved.

Example.—When a mixture of two volumes of hydrogen with one of oxygen (explosive mixture) is ignited, the two substances combine with great evolution of heat to form water vapour, which condenses to water on cooling. The equation for this reaction is



That is to say: 137,000 cal. are set free by the combination of 4 gm. of gaseous hydrogen with 32 gm. of gaseous oxygen to form liquid water. This includes the work performed on the system by the external pressure on account of the decrease of volume. If we wish to know the heat of combination for the process

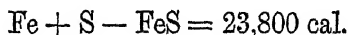


we must subtract from 137,000 cal. the latent heat of vaporization of the water (i.e. 19,400 cal.) which was liberated during the condensation.

At the end of the reaction the quantity Q of heat developed plus the work $p \Delta V$ performed is equal to the decrease of the internal energy

* Gr., *endon*, within.

U of the system. Hence thermochemical equations are often written in the form



The algebraic sum of the amount of work performed and the quantity of heat developed (each either positive or negative) is the change of the total energy of the system.

Particular interest attaches to those chemical reactions (combustions) in which a substance combines with oxygen, since they are simple to carry out experimentally and the quantities of heat developed are as a rule very great. In this case the heat of reaction is called the **heat of combustion**. Although both oxygen and the substance are involved in the development of heat, it is usual to speak merely of the heat of combustion of the substance.

In physics and engineering heats of combustion are often referred to 1 gm. of the substance instead of to the quantities expressed in the chemical equation. Thus, for example, 34,300 cal. are produced by the combination of 1 gm. of hydrogen with the corresponding quantity of oxygen to form liquid water. We will define this value as the heat of combustion of hydrogen.

The measurement of heats of combustion is carried out in many cases inside a *calorimetric bomb*. This consists of a completely air-tight vessel made of steel and covered on the inside with platinum or enamel. If the substance to be investigated is gaseous, the bomb is filled at about 25 atm. with a mixture of this gas with the exact quantity of oxygen necessary for its combustion. An electric spark is then allowed to pass inside the vessel between the wall and an insulated platinum wire; this starts the explosive combustion.

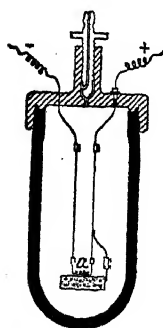


Fig. 20.—Berthelot's Bomb Calorimeter

There are two reasons for carrying out the process with the mixture under pressure: (1) in order to have as large a mass as possible in a small volume and (2) in order that the combustion may proceed to completion.

During the combustion the bomb is placed in a water calorimeter. The heat developed raises the temperature of the bomb and the water. The water equivalent (p. 21) of the former being known, the quantity of heat set free can be calculated from the observed rise in temperature by methods already explained.

If the substance under investigation is solid or liquid, it is suspended inside the bomb in a platinum spoon (fig. 20), the remainder of the interior being full of oxygen. The combustion is then started by means of a platinum spiral which is made red hot by an electric current.

The determination of heats of combustion is of very great practical importance, because the value of substances as fuel depends primarily upon their heats of combustion.

In the case of an allotropic substance (i.e. a substance which can exist in different modifications), the heat of combustion is different for each modification. Thus, for example, the heat of combustion (per gm.)

of carbon to carbon dioxide is 7860 cal. for diamond, 7900 cal. for graphite, and 8000 cal. for amorphous carbon.

Many substances have different degrees of oxidation. In such cases it is necessary to specify which degree is attained in the combustion. For instance, 1 gm. carbon burns to carbon monoxide with development of 2180 cal., but to carbon dioxide with development of 8000 cal. If the combustion of carbon is controlled in such a manner that it first gives carbon monoxide and then this burns to carbon dioxide, the first stage of the process develops 2180 cal. and the second 5820 cal. Thus the total is once again 8000 cal.

It is therefore often possible, in cases where the heat of combustion of a substance cannot be determined directly, to carry out the determination by an indirect method. For instance, it is practically impossible to burn carbon to pure carbon monoxide; hence the corresponding quantity of heat developed cannot be measured directly. The following procedure is therefore adopted: the heats of combustion of carbon and of carbon monoxide to the dioxide are measured directly and the difference taken.

It is a general law that the heat of reaction of several substances taking part in a process depends only upon the end products and not at all upon the way in which these are produced.

It is therefore possible, by the combination of suitable and easily measurable chemical reactions, to calculate heats of reaction which are otherwise only obtainable with difficulty. The knowledge of such heats of reaction is of decisive importance for the calculation of the course of chemical processes. For instance, the heat of transformation of diamond into graphite, which could never be determined directly on account of the extreme slowness of the change, has been found by means of the heats of combustion (NERNST). According to the data given above it is equal to 40 cal. per gm.

Heat of Neutralization.—One heat of reaction which is often determined experimentally is that set free by the mutual neutralization of an acid with a base. It is known as the *heat of neutralization*. The heat of formation of the salt produced by the neutralization can be obtained from it. The measurements are best carried out in a Bunsen ice calorimeter (see p. 69).

13. Application of the Laws of Thermodynamics to Chemical Processes.

1. **The so-called Berthelot Principle.**—When a chemical process is allowed to take place in a calorimeter without performance of external work, a certain heat of reaction, i.e. an absorption or production of a quantity dQ of heat is observed. This is given by

$$JdQ = dU;$$

where dQ is to be reckoned as positive when heat is absorbed and vice versa. A decrease of U thus corresponds to a negative value of dQ , which is then taken to represent a development of heat.

Observation shows that many of the more vigorous chemical processes develop a large quantity of heat. For example, more heat is developed when sodium oxide combines with sulphur trioxide to give sodium sulphate than when the same substance combines with carbon dioxide to give the carbonate. It was once believed that a measure of chemical affinity had been discovered in the heat of reaction. In 1867 BERTHELOT* propounded the rule which is known by his name and which states that of all the possible chemical reactions the one accompanied by the greatest development of heat will occur. He had to exclude changes of state, however. There were also obvious deviations from the rule.

2. Free and Bound Energy.—Unless specially controlled, a chemical process in general takes place irreversibly. In order to account for the deviations from Berthelot's rule, it is necessary to conduct the process reversibly. This can be done by making it perform external work, such as electrical work in a voltaic element, the chemical processes in which can be reversed by expenditure of the same amount of work, or osmotic work in the case of processes in solution, and so on. We have then in general

$$JdQ = JTdS = dU + PdV$$

where PdV represents the external work of all kinds (see p. 142). If the process is *isothermal* (i.e. if there is thermal contact with a large heat reservoir) the external work done, which is given by

$$dA = PdV = -dU + JTdS = -d(U - JTS) = -dH$$

is equal to the decrease of a quantity

$$H = U - JTS.$$

Since the greatest possible amount of work is obtained when the process is conducted reversibly, this decrease of the function H is the maximum amount of work which the process can yield. In 1883 VAN'T HOFF recognized this to be the true measure of chemical affinity. Thus we see that the whole of the decrease of the internal energy U is not obtainable as useful work, but only the part H . The function H is therefore called the *free energy* of the system (HELMHOLTZ), while the other part JTS is called the *bound energy*, because it cannot be obtained in useful form. Thus the total internal energy is composed of these two parts:

$$U = H + JTS.$$

* MARCELLIN BERTHELOT (1827-1907) of Paris, famous chemist.

When a process is conducted isothermally and reversibly the amount of work it performs is given by

$$P dV = - dH.$$

There is also a simultaneous heat of reaction, given by

$$J dQ = JT dS$$

and equal to the change of the bound energy.

Since the entropy increases, *spontaneous processes must cause H to decrease*; that is to say, they must be capable of performing external work. It depends entirely upon the conditions whether this decrease of H is really obtained as work or not. If not, there is an equivalent heat of reaction developed by the system. On the other hand, a process accompanied by an increase of free energy H necessitates the expenditure of external work; such a process never occurs spontaneously. At the same time alterations of the bound energy can cause further heats of reaction either positive or negative.

A few examples may be given by way of illustration.

I. When a salt is dissolved work is performed by the solution pressure P. If the quantity passing into solution is dV , the work done is PdV ; this can be obtained in useful form by a suitable device, say with the help of a semi-permeable membrane. It is equal to the decrease dH of free energy. At the same time the change of state of aggregation causes an alteration of the bound energy, which tends to cause a fall of temperature and for isothermal solution requires the addition of a quantity dQ_1 of heat. If the decrease of free energy is not made to do external work, an equivalent quantity dQ_2 of heat is developed. This is what happens when the salt is dissolved in water without special control. The whole heat absorbed is then

$$dQ = dQ_1 - dQ_2.$$

Thus it is impossible to make any general statement as to whether dQ will be positive or negative. This depends upon whether $dQ_1 \geq dQ_2$ in any particular case. There is usually a fall in temperature when a salt is dissolved, i.e. the isothermal process necessitates addition of heat (dQ positive). This indicates that the increase of the bound energy due to the liquefaction of the salt outweighs the decrease of the free energy.

II. There is a considerable evolution of heat when sulphuric acid is dissolved in water, because the great chemical affinity means a great decrease of free energy, which, when not made to do work, appears as heat. Thus we have a great evolution of heat, i.e. negative dQ when the process is isothermal. When sulphuric acid is mixed with snow, the chemical reaction is accompanied by a melting of the latter. This change of state causes the bound energy to increase more than the free energy decreases, so that on the whole the process causes a cooling or when isothermal requires the addition of heat. On account of the change of state of aggregation of the water, sulphuric acid and ice form a powerful freezing mixture. Similarly in the case salt + water the total internal energy U of the mixture increases during the chemical process. But the free energy always decreases. During the dilution of sulphuric acid with water both the free energy H and the internal energy U decrease, because there is no increase of the bound

energy owing to change of state of aggregation to mask the decrease of the free energy.

We see from these examples that the so-called Berthelot principle only possesses limited validity, namely, for those cases in which there is no change of the bound energy. Such a change may be caused not only by change of state of aggregation but also by dissociation, change of crystal structure, molecular rearrangement, change of specific heat, &c.

III. When current is taken from a voltaic element, the decrease of free energy accompanying the chemical process is made to perform useful electrical work, such as can be employed to drive a motor or to raise weights, i.e. to do mechanical work. The total process is then reversible and there is no heat effect in the element. This method is the one most used to determine the maximum work H . But in addition to the actual chemical reaction, accompanying processes may give rise to a change of the bound energy, in which case a positive or negative amount of heat will be developed. If the electric current is used to produce heat in a wire, the process becomes irreversible. The same is true if the element has an internal resistance against which work is lost. In this case the equivalent quantity of heat is produced in the element.

In order to make full use of the capacity of a chemical process to perform work, it must be conducted reversibly. This necessitates its being slowed up to an infinitesimally small velocity. The reaction must be conducted in such a way that no excess velocity is imparted to the molecules. In an irreversible process the reacting molecules rush together, as it were, unimpeded. Their kinetic energy so obtained is transformed irreversibly into heat.

For the numberless applications of these principles the reader must be referred once more to a special work on chemical thermodynamics, one of the branches of physical chemistry.

14. The Nernst Heat Theorem

According to the preceding paragraph the internal energy U of a system is equal to the sum of the free energy H (the maximum work) and the bound energy JTS , i.e.

$$U = H + JTS.$$

Both the internal energy and also the maximum work are dependent upon the temperature. For $T = 0$, the equation shows that $U = H$. Now experiment shows that in reactions between pure solids and liquids the difference between U and H is only small and that it only varies very little at low temperatures. This led NERNST to assume that at the absolute zero U and H are not only equal but that *their values approach each other asymptotically*, i.e.

$$\lim_{T \rightarrow 0} \frac{dU}{dT} = \lim_{T \rightarrow 0} \frac{dH}{dT} \quad (\text{for } T = 0)$$

(see fig. 21). This is the NERNST heat theorem (1906). According to the equation given above the theorem can also be formulated as follows:

In the neighbourhood of the absolute zero all processes take place without change of entropy; all processes are then reversible, i.e.

$$\lim_{T \rightarrow 0} \Delta S = 0.$$

This means further that no property of a body alters appreciably in the neighbourhood of the absolute zero; indeed even above the absolute zero the alterations are only very small. We conclude also that the volume and pressure of gases are independent of the temperature in the neighbourhood of the absolute zero (*degeneration of gases*).

The NERNST heat theorem has extremely important applications, because with its help the quantity H can be calculated from purely thermal data. For this purpose it is necessary to know the behaviour of U with change of temperature at very low temperatures, i.e. in general the behaviour of the specific heat. Even at easily attainable temperatures the condition

$$\frac{dH}{dT} = \frac{dU}{dT} = 0$$

is often fulfilled; it is generally not necessary to go below 100° abs.

If the vapour pressure curves of

the reagents be known, it is then possible to calculate the course, the temperature dependence and the equilibrium of any chemical process.

$$\text{If} \quad U = U_0 + \beta T^2$$

be known as a function of T , then

$$H = U_0 - \beta T^2$$

is a close enough approximation for many purposes.

The heat theorem has achieved extraordinary success in the treatment of numerous problems and is therefore often called the *third law of thermodynamics*. It may be stated in a form analogous to the first two laws:

It is impossible to attain the absolute zero by any process whatsoever.

As an example of the application of the heat theorem we may mention the calculation of the transition temperature T_0 of monoclinic into rhombic sulphur. At this temperature the two modifications are in equilibrium and the affinity H is therefore zero. Measurements of the specific heats of the two modifications at different temperatures down to 83° abs. give

$$U = 1.57 + 1.15 \cdot 10^{-5} T^2.$$

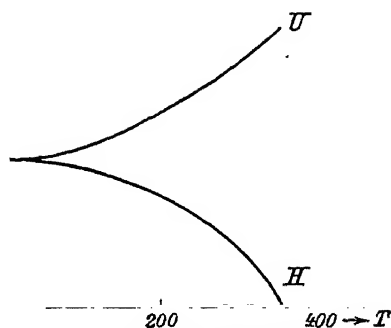


Fig. 21.—Nernst Heat Theorem

From this it follows that $H = 0$ for $T_0 = 369.5^\circ$ abs., whereas the experimentally determined temperature is 368.4° abs. The agreement is excellent. Direct measurements of H are also in very good agreement with the calculated values.

For further details elucidating the significance of the third law of thermodynamics, see Vol. V.

15. The Principle of Le Chatelier

To conclude this general discussion we shall now explain a principle which, though not so far-reaching nor so *quantitative* as the second law of thermodynamics, indicates the direction of a process taking place in a system. It applies only to processes induced by some other primary process in the system or by some external influence. The principle was first enunciated by LE CHATELIER* in 1884, and more thoroughly followed up and established by BRAUN† a few years later. It states:

Every process caused by an external influence or by a primary process in a system takes place in such a direction that it tends to oppose the alteration of the system produced by the external influence or primary process.

Thus when a primary process or influence A gives rise to a process B in a system, the process B protects the system against the primary disturbance, i.e. makes the system more resistant to the change which would otherwise be produced. By means of the process B the system defends itself, as it were, against the process A and tends to weaken its effect. The system is loth to quit the state in which it finds itself and exerts a resistance of inertia against any change.

Examples.—1. The mechanical resistance of inertia exerted by every mass against any change of the magnitude or direction of its motion is a characteristic example. But analogous cases are met with in all the other branches of physics.

2. We increase the external pressure upon a body so as to tend to decrease its volume (influence A). The result is a change of temperature (process B) of such a nature as to tend to increase the volume again. That is to say, bodies which expand on heating have their temperatures raised by compression; bodies which contract on heating (e.g. water below 4° C.) have their temperatures lowered by compression.

3. In the same way rods and wires which lengthen on heating become cooler by extension; those which shorten on heating (loaded rubber tube) become hotter under the same treatment.

4. When heat is added to a mixture of water and ice, the latter melts and thus prevents the rise of temperature which would otherwise occur.

5. Consider two substances in chemical equilibrium. When heat is added, the reaction will proceed in the direction in which heat is absorbed, thus tending to cool the system. Hence rise of temperature favours the decomposition of compounds formed by exothermic reactions (i.e. with evolution of heat), and also the formation of endothermic compounds.

* H. L. LE CHATELIER (born 1850), French investigator, carried out valuable theoretical and practical work in thermodynamics.

† K. FERD. BRAUN (1850–1918), Professor at Strasbourg; in recognition of his valuable work in wireless telegraphy the NOBEL prize in Physics was divided between him and MARCONI in 1909. He died in the United States, where he was staying at the outbreak of the European War and was interned.

6. An increase of pressure favours those changes of form, transformations of molecular and crystalline structure, dissociations, &c., which are accompanied by a decrease of volume, because an increase of volume would increase the pressure still further. For this reason ice melts when the pressure is increased (p. 72) and its freezing-point is lowered. Most other substances are denser in the solid state than in the liquid; their melting-point is therefore raised by increase of pressure.

7. Consider a solid salt in its saturated solution. When the process of solution is accompanied by absorption of heat, rise of temperature causes more salt to dissolve; in the opposite case it causes more to be deposited.

8. When an electrical conductor is moved in a magnetic field, a current is induced in it. This current is such that the action of the magnetic field upon it urges the conductor in the opposite direction from that in which it is moved (Vol. III). Similarly the current induced in a conductor by the approach of a magnet repels the latter; when induced by the withdrawal of the magnet, the current attracts it. The current due to self induction when a circuit is closed or broken is such as to oppose the change of current (Lenz rule, Vol. III).

9. When an electric current passes through the junction of two metals, the temperature of the junction alters in such a way that the resulting thermo-current tends to weaken the original current (Peltier effect, Vol. III).

10. The passage of an electric current through a salt solution causes a polarization current (Vol. III) in the opposite direction.

A large number of further examples might be adduced. It is easy to understand why the direction of the process involved must in all cases be in harmony with Le Chatelier's principle. If this were not the case, no equilibrium state would be possible. Every incipient process or every external influence would be strengthened by the process to which it gave rise in the system, and this mutual effect would lead to a complete change of the system. A conductor in a magnetic field would go on moving continually once it was disturbed; a magnet would recede continually from a solenoid once it was displaced; a momentary current in a thermoelement would give rise to a continuous current and an ever increasing temperature difference of the junctions, and so on.

The fact that according to the principle of LE CHATELIER a closed system reacts to external influences in such a way as to oppose any change, has been taken as justification for attempts to comprehend and explain mechanistically the wonderful appropriateness of the reactions of a living organism to external influences of a disturbing or hurtful nature. It may be mentioned, however, that the principle is not applicable without restriction to all systems and all possible external influences, but presupposes a certain measure of stability. It does not hold for "trigger" actions, i.e. for processes *released* by primary changes in a system, for example, explosions, reactions started by heating, and so on.

16. Heat Engines

The convertibility of thermal energy into mechanical work is turned to practical use in heat engines. Four forms of these have attained especial importance:

A. **Hot-air Engines**, in which the expansion of an enclosed mass of air produced by supply of heat is used to perform work.

B. Piston or Reciprocating Steam Engines, in which use is made of the fact that water occupies a considerably greater volume in the vapour state than in the liquid (1700 times at 100°C . and 1 atmosphere pressure), and that the pressure of water vapour is increased by rise of temperature.

C. Steam Turbines, in which the kinetic energy of the flowing vapour is converted into mechanical work.

D. Gas Engines, in which an explosive mixture of gas and air is ignited inside a closed cylinder, so that the very hot products of combustion drive back a piston.

A. Hot-air Engines.

The hot-air engine * (fig. 22) has only found application for small motors. The air in a cylinder is alternately heated and cooled. The expansion produced by the heating drives a piston outwards; while the fall of pressure during cooling causes the piston to be driven back again by the external atmospheric pressure.

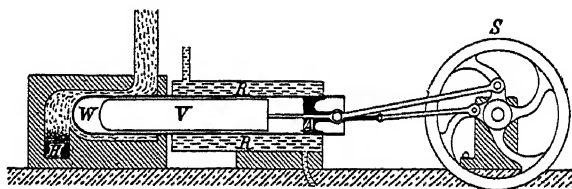


Fig. 22.—Diagram of a Hot-air Engine

The alternate heating and cooling is attained by surrounding one half of the cylinder with the fire box *H* and the other half with a cold-water jacket *R*. A hollow closed metal cylinder, the displacer *V*, half fills the interior of the cylinder of the engine but does not fit tightly against its walls. Hence the air can flow between the cylinder walls and the displacer. When the latter is brought into the cold part of the cylinder, the air passes into the hot part *W* and expands, thus driving out the air-tight piston *A*. When the displacer is brought into the hot part of the cylinder, the air passes into the cold part, is cooled down, and permits the piston to return. The piston rod is jointed to the fly-wheels by a connecting rod, which transforms the backward and forward motion into a rotational motion of the fly-wheel. The displacer rod passes through the piston and is also connected to the fly-wheel by means of a connecting rod: it is thus moved backwards and forwards automatically by the rotation of the fly-wheel.

The disadvantage of this kind of engine lies in the impossibility of increasing the air pressure sufficiently within the range of technically attainable temperatures. For this reason the dimensions of the engine must be very great in comparison to its power.

B. Reciprocating Steam Engines.

I. Mode of Action of Steam Engines.—Water is boiled inside a closed boiler made of iron or steel plates and the vapour prevented from escaping until it has reached a pressure of several atmospheres. The steam under pressure is then conducted into a cylinder closed at

* Invented in 1855 by the Swedish-American engineer JOHN ERICSSON (1803–89), who was also a successful inventor in other directions.

both ends, in which a piston can move backwards and forwards. The steam enters the cylinder on the one side and on the other side of the piston alternately, while in each case the side opposite the steam inlet is simultaneously brought into connexion either with the outer atmosphere (*high-pressure or exhaust steam engine*) or with the condenser (*low-pressure or condensing steam engine*). In the latter case the escaping steam is cooled and condensed to water. The steam inlet and outlet are regulated by the automatic *steam distribution*.

Steam Distribution.*—This takes the form either of *slide-valve distribution* or *distribution by valves of other types*, the latter being used chiefly in high-power

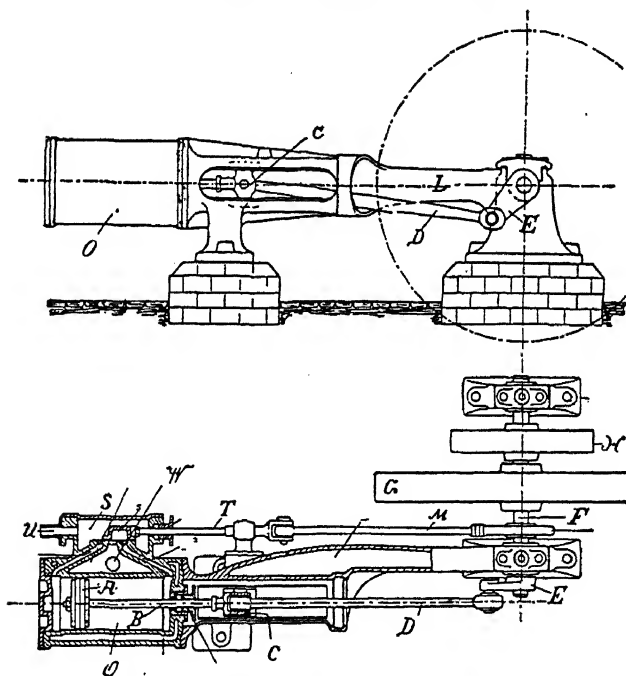


Fig. 23.—Single-cylinder Steam Engine with Simple Slide-valve Control

engines. The mode of operation of a slide valve and the whole action of a steam engine can be seen from fig. 23, which represents a horizontal steam engine with slide-valve control. The slide-valve mechanism is drawn again in detail in fig. 24. The steam comes from the boiler through the tube U. The slide-valve mechanism consists of the *slide casing* S in which the actual slide (D-slide) reciprocates. It glides, hollow side down, upon a plane surface attached to the cylinder. This surface has three holes bored in it: the upper one in fig. 24 leads to the upper part and the lower one to the lower part of the cylinder, while the middle boring is connected to the exhaust pipe W.

* The first automatic steam distribution is said to have been invented about 1717 by the boy HUMPHREY PORTER. The essential parts of the modern steam engine: steam distribution with eccentric sheave, condenser, fly-wheel, governor, &c., were described by JAMES WATT (1736-1819) in the course of work extending over many years from 1765 onwards.

When the slide is in the position shown in fig. 23, the steam entering by way of U can pass through the left-hand passage into the left-hand part of the cylinder O. It presses upon the piston A and drives it to the right. At the same time the steam on the right of the piston in the other part of the cylinder is able to escape through the cavity in the D-slide into the exhaust pipe W.

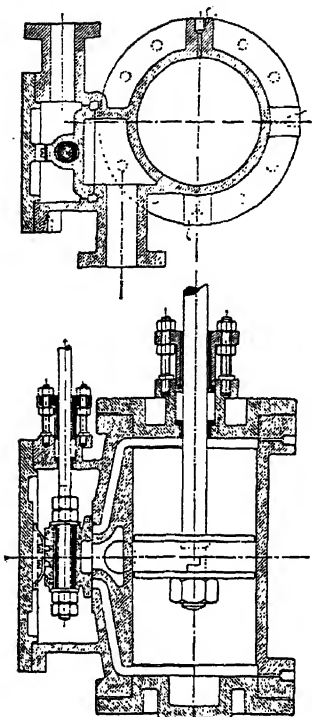


Fig. 24.—Slide-valve Mechanism

In the upper part of the figure there are indicated, in order from above downwards: lubricating hole; indicator socket; socket for drain cock.

The piston A is connected with the piston rod B. This is constrained to move in a straight line by the cross-head C which travels between two guides. One end of the connecting rod D is jointed to the cross-head and the other to the crank web E. Thus the backward and forward motion of the piston is transformed into rotational motion of the crank shaft F and the fly-wheel G. The crank shaft also carries the eccentric sheave H, i.e. a circular disc attached to the shaft in such a way that its axis of rotation does not pass through its centre. The eccentric sheave, which acts exactly as a crank or cam, rotates within a ring bearing (the eccentric strap). To this is attached the eccentric rod M, which is jointed at the other end to the valve spindle T. When the crank shaft rotates the eccentric sheave moves the eccentric rod backwards and forwards, and this motion is transmitted by the valve spindle to the slide valve. The eccentric sheave is turned through 90° on the shaft relative to the crank web E, so that the slide valve is moving with maximum speed in its mean position when the piston is at rest at the end of the cylinder. Similarly the slide valve is at its maximum displacement and approximately at rest when the piston is moving in the middle of the cylinder.

Boilers.—The steam is generated in a boiler, which is usually housed in a special room away from the engine. There are various different types of boiler

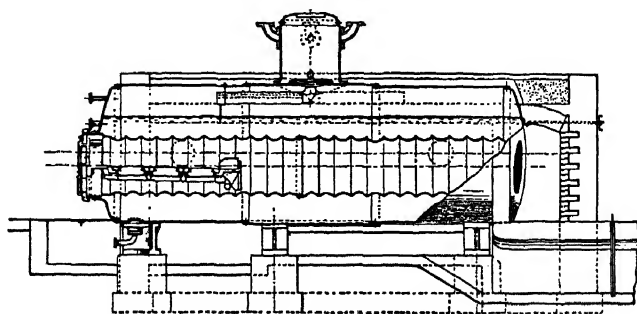


Fig. 25.—Single-flue Tank Boiler with Corrugated Flue

construction. Fig. 25 shows a *single-flue tank boiler*. Through the interior of the cylindrical tank passes a wide and generally corrugated tube forming the space

for the firing. Its front part is divided by the fire bars into two parts, the upper one being occupied by the fuel and the flames and combustion products, while the lower serves as ashpit and inlet for the necessary air. The boiler is enclosed in a wall provided with special flues through which the hot gaseous products of combustion pass, in order that they may remain as long as possible in contact with the surface of the boiler before they pass into the chimney by way of the subterranean flue. The boiler must be filled with water over the furnace flue. In order that the steam may leave in as dry a condition as possible, i.e. without sweeping liquid water along with it, the boiler is provided with a

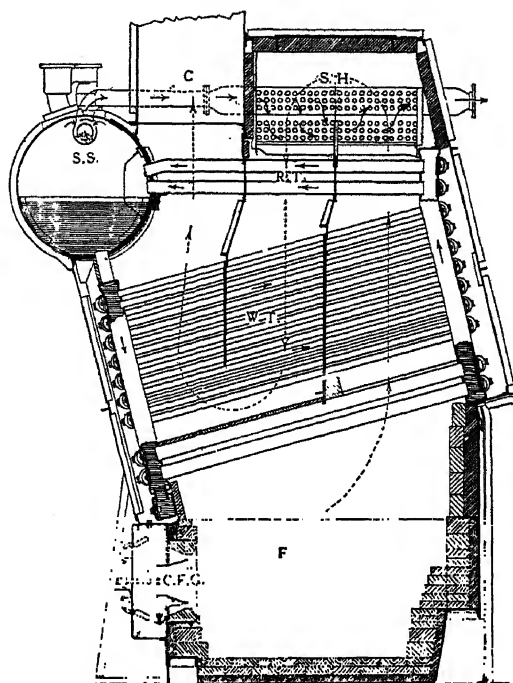


Fig. 26.—Babcock and Wilcox Boiler with Superheater, fitted for Oil-firing, for mail and passenger vessels

S.S. Steam space. W.T. Water-tubes. F. Furnace. R.T. Return tubes.
S.H. Superheater. C. Chimney. O.F.G. Oil-firing gear.

steam dome from which the steam passes through pipes to the actual steam engine.

In *furnace-tube boilers* the furnace gases pass through a boiler in many separate tubes (e.g. in locomotives, torpedo boats, &c.). In *water-tube boilers* (fig. 26) the actual boiler consists almost entirely of a system of tubes which are surrounded outside by the furnace flames and gases. In the best plants of this type, up to 85 per cent of the heat of combustion of the fuel is transferred to the boiler water.

The steam leaving the boiler is often heated further without increase of pressure to a temperature above the boiling-point corresponding to the working pressure, so that it enters the cylinder completely dry and undergoes a greater expansion (*superheated steam*). The chief advantages of superheated steam are of a practical nature: it does not conduct heat nearly so well as wet steam, and is therefore much less sensitive to the cooling influence of the internal surface of

the engine. Hence the use of superheated steam allows of a considerable economy of water and fuel without loss of power.

The endeavours (based upon thermodynamical reasoning, p. 122) to use the highest possible initial temperatures in heat engines are of great physical interest and also of ever-increasing practical importance. In one of these, the *Benson method*, the production of steam takes place in the critical state (205 atm.; 374°C.), in which the density of the saturated vapour is equal to that of the water, and the liquid passes directly into the vapour state without the formation of a mixture. This also has the considerable advantage that the latent heat of vaporization is zero. The production of vapour takes place in the simple manner represented diagrammatically in fig. 27. The water is compressed by means of high-pressure pumps *a* into a system of tubes at 230 atm. There it is heated to 374°C. , so as to vaporize it. Further supply of heat causes the vapour to become superheated. This superheated vapour is conducted to the engine and finally passes back to the boiler as condensate. In fig. 27 the curve showing the volume

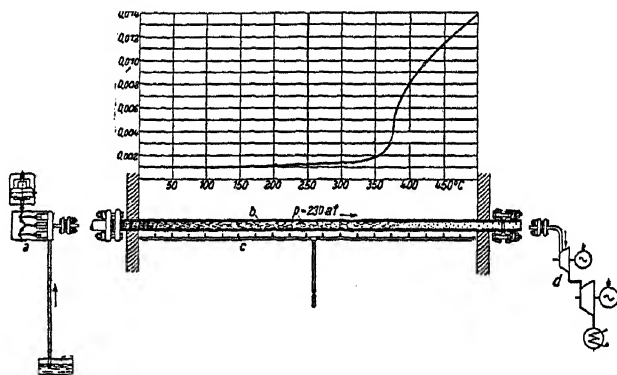


Fig. 27.—Principle of the Benson Method. (Ordinates represent specific volumes)

of the water and vapour as a function of the temperature is shown above the tube in which the vaporization takes place. It is seen that even before the critical temperature is reached there is already a loosening of the molecular texture of the water and a consequent increase of volume to three times its original value. The volume then increases rapidly during superheating, as is to be expected of the gaseous state. On account of the technical difficulties involved such highly compressed vapour is used almost exclusively in steam turbines (p. 165).

Condenser.—If the exhaust steam from the cylinder escapes freely into the air, it has to overcome the back pressure of the atmosphere; but if it is allowed to escape into a vacuum, this back pressure is no longer present. The condenser serves to produce a vacuum. It is a special vessel into which the exhaust steam flows and is condensed by means of cold water. The cooling water may either be sprayed directly into the condenser, i.e. mixed with the steam (*spray or mixing condenser*) or made to flow through numerous tubes passing through it. In the latter case the exhaust steam from the engine condenses on the surface of the tube system (*surface condenser*).

Expansion.—The steam enters the cylinder at approximately the same pressure as that in the boiler. If it were allowed to flow in freely during the whole of the piston stroke, a volume equal to the whole volume of the cylinder would be required. During the return stroke of the piston this highly compressed steam would escape into the atmosphere. But highly compressed steam is still able to

do work on account of its compression, so that this escape would represent a waste of work, i.e. a waste of fuel. For this reason the steam inlet is closed before the piston has completed its stroke and the steam is thus allowed to *expand*. In this way use is made of the work done during expansion. Theoretically the energy of the steam would be fully used if it could expand to atmospheric pressure or to the pressure in the condenser. This, however, would necessitate the use of impracticably long cylinders (p. 115).

Compound Engines.—In these the steam is enabled to undergo a very large expansion, and a better utilization of its energy is therefore attained. The steam, which has expanded in the first cylinder to about half its original pressure, i.e. to twice its original volume, is not allowed to escape directly into the condenser, but is conducted into a second cylinder of greater cross-section in which it yields more work by further expansion. The steam is thus enabled to expand from its original volume to that of the larger cylinder.

Fig. 28 shows a *two-stage compound engine*. Here the two cylinders I and II are situated one above the other. The steam enters the lower part of the *high-pressure cylinder I* at boiler pressure through the pipe Z_1 and the slide-valve casing. It thus raises the upper piston. The steam still in the upper part of I leaves through the upper slide-valve casing and passes by way of Z_2 into the lower slide-valve casing, whence it enters the lower part of the *low-pressure cylinder II*. The expanding steam thus lifts the lower piston in the same direction as the upper one. The exhaust steam from II passes out through A into the condenser. (In a triple-expansion engine it first does work in a third, still larger cylinder.) When, as in fig. 28, both pistons are attached to the same piston rod, the engine is called a *tandem engine*.

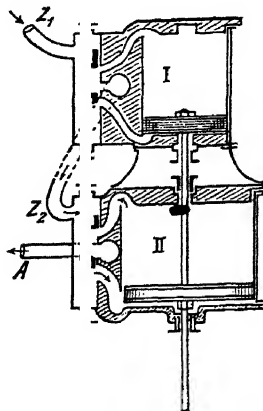


Fig. 28.—Diagram of a Two-stage Compound Engine

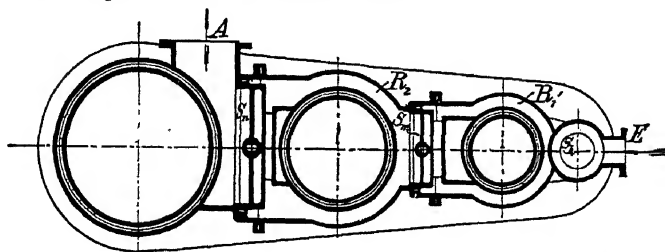


Fig. 29.—Low-pressure, Intermediate-pressure, and High-pressure Cylinders (in order from left to right in diagram)

The cylinders are usually arranged side by side, as in the plan shown in fig. 29. The cylindrical shaped slide valve S_h lets the steam from E into the high-pressure cylinder. After it has expanded here it passes by way of the slide valve S_m into the intermediate-pressure cylinder and finally through the slide valve S_n into the low-pressure cylinder. From here it escapes through A into the condenser. The motion of each of the three pistons is transmitted by means of a connecting rod to a special crank or eccentric on a common shaft.

II. Calculation of the Work yielded by a Steam Engine.—The work performed by the piston of a steam engine can be calculated from the magnitude of the total thrust P exerted and the distance h through which it acts. Here h

is the length of the stroke of the piston, i.e. the length of the cylinder minus the thickness of the piston. The work done during each stroke is therefore $W = Ph$. The force P is itself equal to the product of the cross-sectional area A of the cylinder or of the piston face, and the steam pressure p per unit area, i.e. $P = Ap$.

The pressure in kg. wt. per 1 cm.² of the piston surface is equal to the number of technical atmospheres pressure in the boiler minus the back pressure of the

Fig. 30.—Work Diagram for Full Admission

Fig. 31.—Work Diagram with Expansion

exhaust steam on the other side of the piston. In the simplest case, where the steam escapes into a completely evacuated condenser, p is equal to the pressure read off on the pressure gauge of the boiler plus one atmosphere. Hence the work done in one stroke of the piston is $W = Aph$. The product Ah is equal to the volume V occupied by the vapour in the cylinder and therefore $W = pV$.

In a piston steam engine working with full admission, i.e. in which the steam exerts its full pressure on the piston during the whole stroke, the work is equal to the product of the steam pressure and the volume swept out by the piston. This may be represented, as in fig. 30, by the area of a rectangle, one side of which represents the volume and the other the pressure (work diagram).

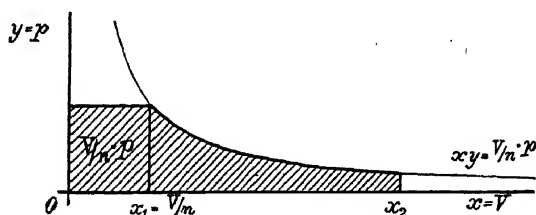


Fig. 32.—Theoretical Work Diagram

In an engine working with expansion, i.e. in which the steam inlet is cut off, for example, when the stroke is half completed, we have the conditions shown in fig. 31. The work W_1 during the steam admission is represented by a rectangle, one side of which represents the half volume swept out by the piston and the other the pressure. Then follows the expansion. We will assume for the purposes of calculation that the pressure decreases in accordance with Boyle's law.* The area representing the expansion work is then bounded above by a portion of a rectangular hyperbola. The pressure of the exhaust is half as great as that of the boiler steam. The area of the figure representing the expansion work can be calculated easily with the help of the infinitesimal calculus.

* If the expansion were adiabatic, we should have to use the equation of Poisson's law. On account of the gains and losses of heat through the cylinder walls, the actual behaviour of the steam will be intermediate between the two laws.

We will perform the calculation for the general case where the steam inlet is cut off when $1/n$ of the total volume has been filled. The shaded area in fig. 32 represents the work performed by the piston during one stroke. The part marked $pV/n = W_1$ gives the admission work. The scale of the figure is so chosen that this part is a square, the one side representing the volume V/n which is filled at full steam pressure, and the other the magnitude of this admission pressure.

The process of expansion is represented by a rectangular hyperbola with the equation

$$xy = \frac{V}{n}p.$$

The abscissa x_2 gives the total volume of cylinder.

The **expansion work** is determined by the area of the figure bounded by the axis of abscissæ, the ordinates to x_1 and x_2 , and the arc of the hyperbola intercepted between them. This area is given by the general formula

$$W_1 = \int_{x_1}^{x_2} y dx.$$

Substituting the value of y from the equation of the hyperbola, we obtain

$$W_2 = \frac{V}{n}p \int_{x_1}^{x_2} \frac{dx}{x} = \frac{V}{n}p (\log_e x_2 - \log_e x_1) = \frac{V}{n}p \log_e \frac{x_2}{x_1}.$$

Now $x_2 = nx_1$, i.e. $x_2/x_1 = n$. Therefore the expansion work is

$$W_2 = \frac{V}{n}p \log_e n.$$

The total work W done by the piston during one stroke is the sum of the admission work W_1 and the expansion work W_2 , i.e.

$$W = \frac{V}{n}p + \frac{V}{n}p \log_e n = \frac{V}{n}p (1 + \log_e n).$$

Here V/n is the quantity of steam admitted to the cylinder, i.e. the amount actually taken from the boiler. Putting this equal to V' , the expression simplifies to

$$W = V'p (1 + \log_e n).$$

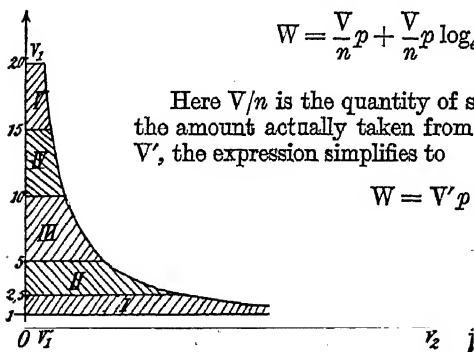


Fig. 33.—Effect of Initial Pressure upon the Output

Under certain conditions, namely, when $n > e$, the second part of the work is greater than the first. In an engine working without expansion the second part is entirely lost.

Advantage of High Steam Pressure.—From the last expression for W it follows that the greater the initial pressure p and the greater n , the greater the work yielded by a given volume of steam. This is also clear from fig. 33, in which it is assumed that a certain volume V of steam enters under the excess pressure (i.e. pressure difference between the two sides of the piston) of 20 atm. and expands to atmospheric pressure. The different parts of the shaded area represent the amounts of work performed by the steam in the cylinder between the respective pressures. Thus it performs the amount I of work if it enters at 2.5 atm. and leaves at 1 atm. If the pressure on entry is 5 atm., the extra amount II of

work is obtained. Similarly the additional amounts III, IV and V of work are obtained by raising the initial pressure to 10, 15 and 20 atm. respectively.

Now it is true that a greater supply of heat is required in order to produce a higher steam pressure in the boiler; but the extra amount of fuel consumed for this purpose is only small in comparison with that used up in vaporizing the water in the first place. The use of a higher pressure therefore enables a higher efficiency to be attained. When the steam pressure is still further raised, the corresponding gain of work does not go on increasing in the same degree; at higher pressures the areas added are only narrow. The engineering difficulties of boiler construction and prevention of leakage in the engine also increase extraordinarily as the pressure and temperature of the steam are raised. Hence pressures higher than 15 atm. were formerly seldom employed.

Nowadays these difficulties have been overcome, so that pressures of 30 atm. or more are quite practicable. High-pressure plants are also built for 200 atm. or more (p. 158). Such high pressures and admission temperatures of 450° – 475° C. are mostly used in connexion with steam turbines (see p. 169).

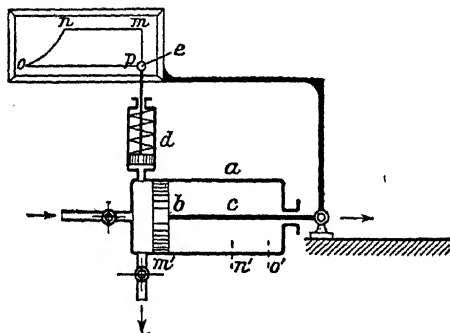


Fig. 34.—Diagram of a Steam-engine Indicator

(Arrows indicate: left, steam inlet; below, steam outlet; right, to the crank)

The fact that the thermal efficiency of a steam engine is increased by raising the initial pressure and lowering the final pressure of the steam also follows at once from the calculations carried out in connexion with the Carnot cycle (p. 115). The higher the initial pressure, the higher the initial temperature T_1 of the working substance; the lower the final pressure, the lower the temperature T_2 of the condenser. The efficiency of the Carnot engine is proportional to the difference $1 - T_2/T_1$. Therefore the efficiency of a steam engine must be increased by raising the initial pressure and lowering the final pressure of the steam.

The Indicator.—In the paragraphs above the work was calculated by purely theoretical considerations, more particularly with the assumption that the pressure of the steam entering the cylinder is the same as that in the boiler and that the expansion takes place in accordance with Boyle's law. In actual fact the pressure conditions in the cylinder do not correspond accurately to the theory. The actual pressure in the cylinder is therefore measured by means of a special device which makes an automatic graphical record of the pressures at every moment of the stroke. This device is called an *indicator*. Its mode of action is shown diagrammatically in fig. 34. The backward and forward motion of the piston b in the cylinder a is transmitted by the piston rod c to a holder for the sheet of paper (in actual instruments usually a rotating drum). The main cylinder is provided with a small side cylinder d , the piston of which pushes against a spiral spring and thus compresses it proportionally to the pressure inside the cylinder. These motions are recorded on the paper by the pencil e .

When the engine is running the pencil moves up and down and the paper moves backwards and forwards (usually with a rotational motion imparted by suitable transmission). Thus the pencil simultaneously records the pressure in the vertical direction and the piston displacement in the horizontal direction. The result is a curve from which the steam pressure can be read off for any position of the piston.

A (closed) curve of this kind is called an **indicator diagram**. The points n and o upon it (fig. 34) correspond to the positions n' and o' of the piston. The diagram gives at once the work done by each stroke of the piston; this is represented by the area enclosed by the curve.

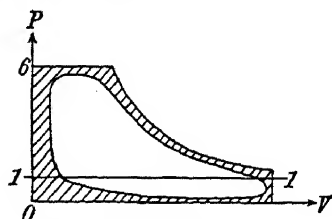


Fig. 35.—Indicator Diagram

Fig. 35 shows both the theoretical work diagram for a steam engine and also the indicator diagram actually obtained. The shaded part shows the difference between the *theoretical* and the *indicated* work; it represents the unavoidable loss of work.

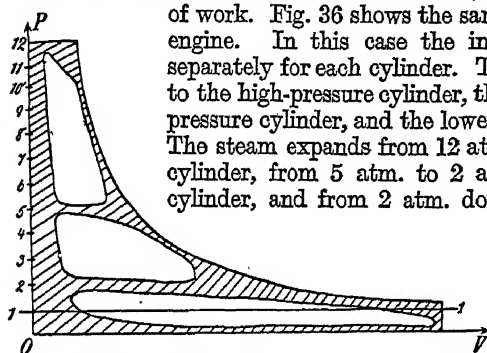


Fig. 36.—Indicator Diagram of a Triple-expansion Engine

Fig. 36 shows the same diagrams for a triple-expansion engine. In this case the indicator diagram must be taken separately for each cylinder. The top unshaded area corresponds to the high-pressure cylinder, the middle one to the intermediate-pressure cylinder, and the lower one to the low-pressure cylinder. The steam expands from 12 atm. to 5 atm. in the high-pressure cylinder, from 5 atm. to 2 atm. in the intermediate-pressure cylinder, and from 2 atm. down to the condenser pressure in the low-pressure cylinder.

The line 1—1 is the so-called *atmospheric line*. The area of the indicator diagram lying below this line represents the work gained by the use of a condenser (p. 155). The shaded part of the figure again gives

the difference between the theoretical and the indicated work.

In order to evaluate the indicator diagram with regard to the work performed per piston stroke, the area enclosed by the curve is represented as the area of an equivalent rectangle upon the same base (see fig. 37). The height p_m of this rectangle is the *mean steam pressure* used in calculating the indicated work.

III. Power and Efficiency of Piston

Steam Engines.—The power of a steam engine is usually expressed in horse-power (h.p.). If the work performed by the piston per stroke (expressed in m. kg. wt.) is known from the indicator diagram, this need only be multiplied by the number of strokes per second, i.e. by twice the number of revolutions of the shaft, and then divided by 75, in order to obtain the **indicated horse-power**. This is designated by i.h.p. Recently preference is being shown for the expression of steam-engine powers in kilowatts (Vol. I).*

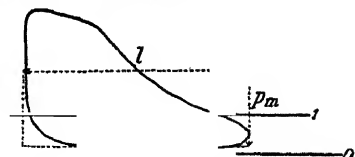


Fig. 37.—The Rectangle of Area equal to that of the Indicator Diagram

* In English engineering the mean effective pressure is measured in pounds per square inch. This has to be multiplied by the area of the piston in square inches and by the length of the piston stroke in feet to find the work done per stroke in foot-pounds. The indicated horse-power is then obtained by multiplying this by the number of strokes per minute and dividing by 33,000.

The **brake horse-power** (b.h.p.) is the power actually delivered by the machine in working. This is measured by means of a brake dynamometer, e.g. Prony's brake (Vol. I).

The ratio of the brake horse-power to the indicated horse-power is called the mechanical efficiency of the engine; it is generally expressed as a percentage. In large well-made steam engines its value may be as high as 90 per cent. If the mechanical efficiency is known, the brake horse-power can be calculated at once from the indicated horse-power as obtained from the indicator diagram.

A steam engine requires between 4 and 20 kg. of steam per horse-power per hour, according to the magnitude of the steam pressure used. This amount can be calculated from the cylinder volume and the speed of revolution, allowance being made for unavoidable losses. From the amount of steam used, it is possible further to calculate the quantity of heat required and also the amount of fuel, and hence finally the cost of running. The average calculated value is about 1 kg. of coal for the production of 8 kg. of steam. Hence in the best steam engines about $\frac{1}{8}$ kg. of coal is required per horse-power hour. In special cases the fuel consumption has been reduced to as low as 0.4 kg. of coal per horse-power hour.

The average heating value of coal is about 8000 Cal. per kg. If, therefore, the whole of this could be converted into mechanical work, it would yield $\frac{1}{8} \cdot 8000 \cdot 425$ m. kg. wt. = $1.7 \cdot 10^6$ m. kg. wt. Now one horse-power hour is only equal to $75 \cdot 60 \cdot 60$ m. kg. wt. = 270,000 m. kg. wt. The ratio of the amount of work actually obtained to the total amount of energy supplied in the form of fuel is called the **economic efficiency** of the engine. In the above mentioned very favourable case it is equal to

$$\frac{75 \cdot 60 \cdot 60}{\frac{1}{8} \cdot 8000 \cdot 425} = 0.16 \text{ or } 16 \text{ per cent.}$$

The economic efficiency of smaller steam engines is much lower than this, and often does not amount to as much as 2 per cent. That is to say, more than 98 per cent of the heat energy liberated by the combustion of the coal is lost.

The theoretical maximum utilization of the thermal energy of the steam is determined (p. 120) by the initial temperature T_1 of admission and the final temperature T_2 of the condenser, and is equal to $(T_1 - T_2)/T_1$. In the case of an engine working at 15 atm. initial pressure, $T_1 = 197^\circ \text{C.} = 197 + 273 = 470^\circ \text{abs.}$ The temperature of the condenser may be taken as $30^\circ \text{C.} = 30 + 273 = 303^\circ \text{abs.}$ Then

$$\frac{T_1 - T_2}{T_1} = \frac{167}{470} = 0.355 \text{ or about } 35 \text{ per cent.}$$

This is the fraction of the heat which the engine could utilize if it worked without any losses due to friction, radiation, &c.

A comparison of the actual and theoretical thermal efficiencies shows that considerably better utilization of the coal is inherently possible than has yet been attained. In the best steam engines not half of the convertible energy of the coal used for the steam generation is actually turned to use.

If the energy of combustion of the coal were not employed for the generation of steam (a method by which the maximum amount obtainable as work is about 35 per cent), but could be converted into work in some other way (e.g. by a direct electrical process), an ideal utilization of 95 per cent would be attained. This is the magnitude of the free energy H of the combustion (NERNST).

C. Steam Turbines.

Principle.—The principle of steam turbines is the conversion of the kinetic energy of a stream of vapour into work. This is effected by allowing the stream to issue from a nozzle and impinge upon a set of

vanes (blades, buckets) fitted on a rotator. The interaction between liquid jets and bucket wheels has already been discussed (Vol. I. p. 355 *et seq.*); the same essential considerations can be transferred at once to jets of steam. Reference should be made to Vol. I for the nomenclature, which will be used below without further explanation. New factors enter in the case of steam turbines on account of the peculiar properties of vapours at very great velocities of flow.

Nozzle Shape.—When vapour flows out of a container at high pressure into another at low pressure through a simple orifice or through a tapering nozzle, the velocity of flow cannot exceed a velocity approximately equal to that of sound (about 450 m. per sec. in the case of

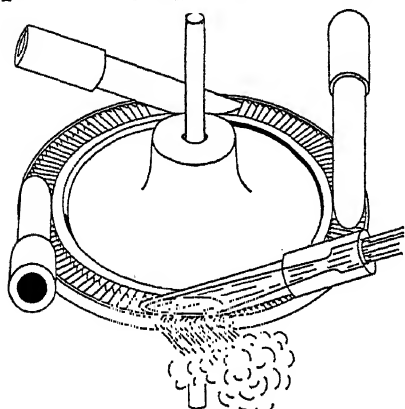


Fig. 38.—Principle of the De Laval Turbine

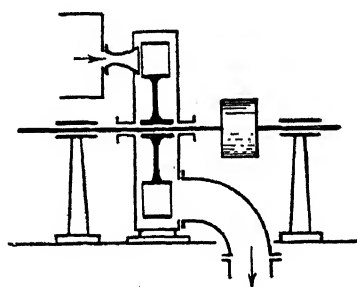


Fig. 39.—Diagram of a Single-stage Impulse Turbine

(Arrows: upper, from boiler; lower, to condenser)

steam), no matter how great may be the pressure difference between the containers. This velocity can only be exceeded without limit by the use of divergent nozzles of a special shape (see, for example, fig. 38); in this case the vapour forms a jet. The nozzles are thus devices in which the pressure of the vapour is transformed into velocity (Vol. I, p. 340).

Speed of Revolution in Turbines.—On thermodynamic grounds it is desirable to use vapour at the highest possible initial pressure and the lowest possible final pressure. The above mentioned attendant difficulties as to jet velocity can be overcome by a suitable nozzle shape. But other difficulties also arise. As stated at p. 355, Vol. I, the utilization of the energy of a jet is most perfect when the velocity of the blades of the rotor is one half of the velocity of the jet. Since now the jet velocity of vapour issuing through a correctly shaped nozzle from 10 atm. initial pressure into 0.2 atm. condenser pressure is about 1100 m. per sec., the peripheral velocity of the rotor would have to be about 500 m. per sec. The first steam turbines (DE LAVAL*), which were built in the manner shown diagrammatically in figs. 38 and 39,

* GUSTAVE DE LAVAL built the first practicable impulse turbine in 1887. Its most important parts are shown in fig. 38.

attained these peripheral velocities at speeds of revolution up to 20,000 per minute. Hence for practical use inconvenient gear transmissions were necessary. Increase of the diameter of the rotor, which of course lowers the speed of revolution for a given linear velocity of the periphery, met with no success on account of technical difficulties.

There are various methods by which, as explained below, this trouble can be overcome.

We may distinguish between the following two types of turbines.

I. Impulse or Constant-pressure Turbines, in which the pressure is the same on exit as on entry (see below). The De Laval turbine belongs to this class.

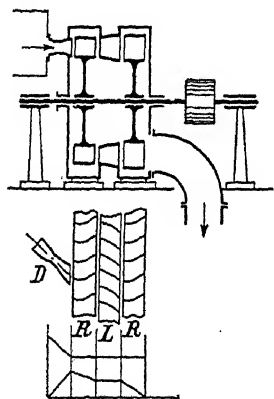


Fig. 40.—Diagram of a Turbine with Two Velocity Stages

(In figure, upper broken line represents pressure of vapour, the lower represents velocity.)

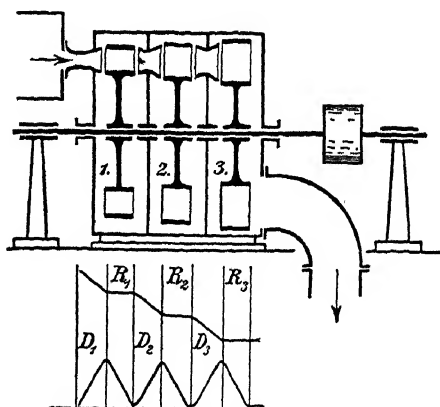


Fig. 41.—Diagram of a Turbine with Three Pressure Stages

(D, nozzle; R, rotor. In figure, upper line, pressure of vapour; lower line, velocity of vapour.)

A. Turbines with Velocity Stages.—If the blades run too slowly, the steam does not impart the whole of the kinetic energy to them, but flows out with a certain fraction of its original velocity. It is then conducted through suitable nozzles or arrangements of blades (guide blades, guide wheel L) into a second rotor R (fig. 40). Both rotors are generally mounted so as to form one wheel (see fig. 40) (Curtis wheel). The pressure in the whole of the casing of this type of turbine (as also in the De Laval type mentioned above) is equal to that of the external atmosphere or of the condenser, this pressure being attained at the mouth of the nozzle where the whole pressure difference is converted into velocity (Vol. I, p. 340). Thus it is only the velocity of the steam which alters during passage through the wheels.

B. Turbines with Pressure Stages.—In order to avoid very high steam velocities, however, the pressure drop can be divided up into several stages, i.e. the steam need not attain the final pressure after passage through one nozzle, but may pass first into a space at inter-

mediate pressure. The steam velocity will then depend upon the pressure difference and can thus be made to have any desired magnitude by suitable choice of the pressure stages. Fig. 41 shows a diagram of such a turbine and also the pressure and velocity variations of the steam.

II. Reaction Turbines.—The pressure fall may be made to occur, not in the nozzles or the fixed guide wheels, but in the rotor wheels themselves, which must then be given a special form. In this case the steam not only gives up its kinetic energy of flow to the blades of the rotor, but also in virtue of its expansion within the rotor it, so to speak, drives the blades back behind it. Since the pressure is greater on the inlet side of the rotor than on the outlet side, this type is sometimes

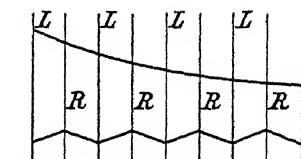


Fig. 42.—Pressure and Velocity Variations in a Parsons Turbine (L, guide wheel; R, rotor)

known as the variable pressure type (PARSONS* turbine). The thrust on the rotors due to this difference of pressure on the two sides must be kept as small as possible or else compensated by special devices. The first of these objects is attained by attaching the rings of blades to drums instead of to separate rotors. A large number of stages (up to 70) are used. Fig. 42 shows the pressure and velocity variations and fig. 43 a sketch of a turbine with three pressure stages. In this type of construction the thrust towards the right upon the rotors is

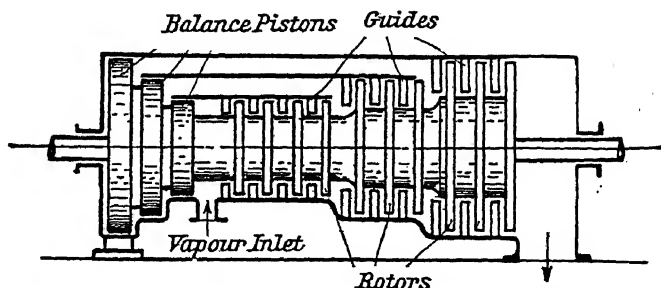


Fig. 43.—Reaction Turbine with Three Stages of Expansion (Diagrammatic)

compensated by means of *balance pistons* which are subjected to a thrust towards the left. Because of their large number of stages, reaction turbines work with very small pressure drops and, since vortices in the vapour are avoided, they have an excellent thermal efficiency.

III. Combination Types of Turbine.—In order not to have too high a pressure (and hence also temperature) in the main part of the turbine, the pressure is allowed to drop as much as possible in the first nozzle, i.e. the first rotor is made in the form of an impulse wheel (generally

* CHARLES PARSONS built the first practicable reaction turbine in 1886 at Newcastle-on-Tyne.

a Curtis wheel with two stages). This is the form in which practically all modern turbines are built. After the Curtis wheel come the remaining stages, the nature of which depends upon the particular type of turbine. Fig. 44 shows the details of a Parsons compound reaction turbine.

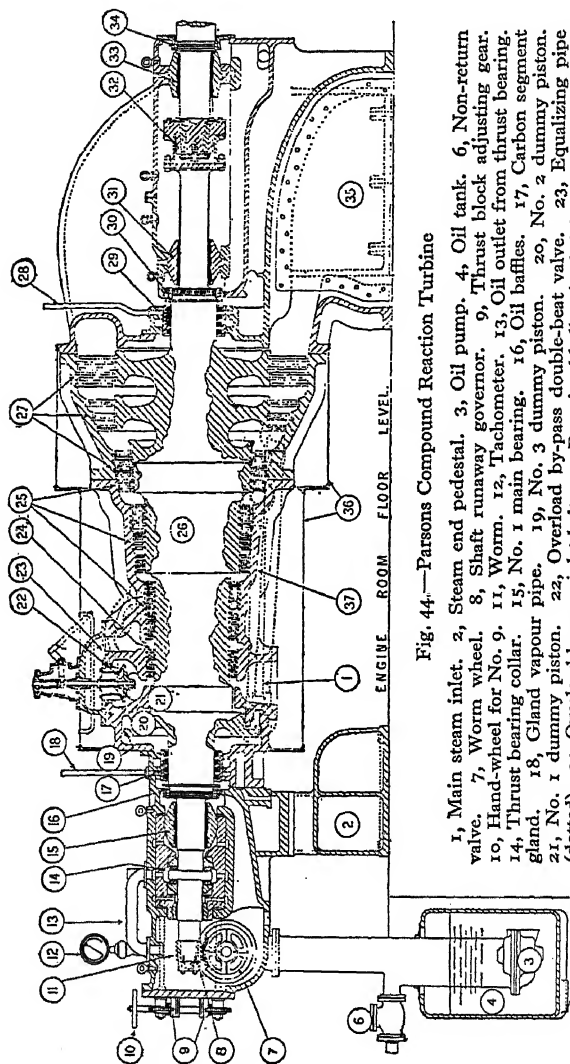


Fig. 44.—Parsons Compound Reaction Turbine

1, Main steam inlet. 2, Steam end pedestal. 3, Oil pump. 4, Oil tank. 6, Non-return valve. 7, Worm wheel. 8, Shaft runaway governor. 9, Thrust block adjusting gear. 10, Hand-wheel for No. 9. 11, Worm. 12, Tachometer. 13, Oil outlet from thrust bearing. 14, Thrust bearing collar. 15, No. 1 main bearing. 16, Oil baffles. 17, Carbon segment gland. 18, Gland vapour pipe. 19, No. 3 dummy piston. 20, No. 2 dummy piston. 21, No. 1 dummy piston. 22, Overload by-pass double-beat valve. 23, Equalizing pipe (dotted). 24, Overload by-pass inlet belt. 25, Reaction blading (end tightened). 26, Turbine shaft. 27, Reaction blading (ordinary radial clearance). 28, Gland vapour pipe. 29, Carbon segment gland. 30, Oil baffles. 31, No. 2 main bearing. 32, Flexible coupling. 33, No. 3 main bearing. 34, Oil baffles. 35, Turbine exhaust. 36, Cylinder lagging. 37, Equalizing pipe (dotted).

Advantages of Steam Turbines.—The main advantages are: simplicity of construction, quiet running, small size, easy starting and many advantages in the matter of attendance. Whereas in steam engines a maximum total efficiency of 16 per cent, or in some cases 17 per cent (p. 164), is attainable, well-built turbines give a total efficiency of 20 per cent; that is to say, 20 per cent of the heating value

of the fuel is converted into work. Thus, steam turbines are more efficient than reciprocating steam engines. Recently attempts have been made to increase the efficiency (as in the case of steam engines) by the use of very high initial temperatures. Whereas large plants usually work with about 30 atm. initial pressure (sometimes with superheating to 425°), modern turbines have been made to work with 100 atm. initial pressure (high-pressure turbines) and about 475° initial temperature. The speed of revolution is usually about 1000–3000 per minute.

D. Gas Engines (Internal-combustion Engines) *

Steam-driven engines involve the conversion of the heat of combustion of the fuel into steam pressure. This not only imposes an upper limit to the initial temperature which can be attained (thus limiting the total efficiency for purely thermodynamic reasons), but it also gives rise to unavoidable working losses which considerably diminish the total efficiency. In gas engines, on the other hand, an explosive mixture of air and fuel gas is ignited in the engine itself and the resulting increase of pressure is converted directly into mechanical work.

The advantages of this procedure are firstly the elimination of a great part of the losses necessarily involved in the indirect method employing the generation of steam, and secondly, the use of very high initial temperatures (generally over 1500° C.) in the thermal process. Consequently it is possible in such motors (more particularly in Diesel engines) to attain a total efficiency of 0.35; that is to say, 35 per cent of the thermal energy liberated by the combustion of the fuel is converted into mechanical work. Thus an engine of this kind has an efficiency twice as great as that of a steam engine. On an average the total efficiency of moderate sized gas engines may be taken as about 0.24.

Gas engines therefore furnish a much more rational solution of the problem of the utilization of thermal energy than do steam engines. The disadvantage of gas engines lies in the fact that their fuel (reckoned per horse-power hour) is in general more expensive than coal. A direct application of coal in gas engines has not yet met with success.

Construction of Gas Engines.—As has already been mentioned above, the principle of the gas engine consists in igniting a combustible or explosive gas mixture under pressure in the cylinder and utilizing the increase of pressure for the performance of mechanical work by means of a piston, as in the steam engine. On account of

* First made on a large scale by the Frenchman R. LENOIR from 1860 onwards. EUGEN and OTTO LANGEN of Deutz built four-stroke motors from 1867. The forms of modern motors for cars and aeroplanes have been evolved as the result of competition between inventors in all the leading engineering countries, since DAIMLER devised the petrol motor at Cannstatt in 1885 and C. BENZ took out the first patent for a petrol automobile in 1886.

the high temperatures involved the cylinder must be cooled. The most common type of engine works on the *four-stroke principle*, i.e. the piston only does work during every fourth stroke, the other three strokes being used respectively for suction, compression and exhaust. The mode of action is shown in fig. 45. In stroke 1 the air-gas mixture is sucked into the cylinder; in stroke 2 it is compressed and ignited (nowadays almost exclusively by means of an electric spark) at top dead centre (generally shortly before); in stroke 3 it is allowed to expand; in stroke 4 the burnt gases are expelled into the outer atmosphere. The inlet and outlet valves are opened and closed at the right moments by suitable mechanism. The portions of the work diagram corresponding to the different phases are also shown in fig. 45. The

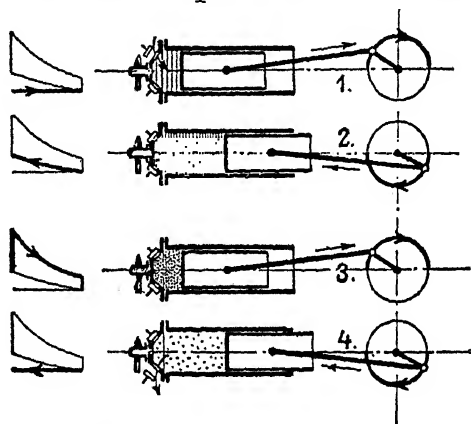


Fig. 45.—Four-stroke Principle

1, Suction. 2, Compression. 3, Working stroke. 4, Exhaust.

disadvantage of this four-stroke action is the uneven force development (fig. 46), since the fly-wheel (which is also necessary here, as in a steam engine) is only propelled every other revolution. The velocity of the crank-shaft is therefore non-uniform and the fly-wheel must be made rather large. To counteract this, several cylinders are usually arranged so as to drive the same shaft (fig. 47); in large engines there are generally two, in smaller ones (e.g. motor-car engines) six or eight. The working strokes of the different cylinders are made to follow one another at intervals equal to the corresponding fraction of the total cycle. Thus, for example, in an eight-cylindrical motor the crank-shaft receives an impulse every quarter revolution.

Two-stroke Engines.—Another method is to build engines which perform work *every second stroke*. The principle is as follows (see fig. 48). The cylinder has exhaust ports, which are closed during the greater part of the stroke by the relatively long piston and are only opened at the end of the stroke when the exhaust is to escape. On account of their rather high pressure the burnt gases rush out rapidly

and are completely removed from the cylinder by compressed air. Shortly before the ports are covered again by the returning piston a new charge of gas mixture is forced into the cylinder by means of

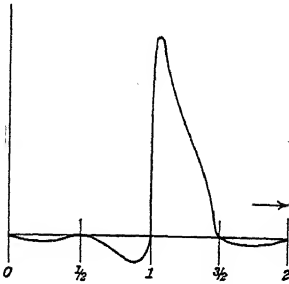


Fig. 46.—Force Transmission to the Crank from a Four-stroke Cylinder

Ordinates, crank force. Abscissæ, revolutions: 0 — $\frac{1}{2}$, suction; $\frac{1}{2}$ — 1, compression; 1 — $\frac{3}{2}$, working stroke; $\frac{3}{2}$ — 2, exhaust.

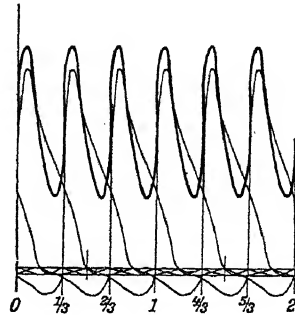


Fig. 47.—Force Transmission to the Crank in a Six-cylindered Motor

(Ordinates, crank force; Abscissæ, revolutions of motor shaft)

special pumps. (In small engines the incoming charge itself is often used for scavenging, i.e. for driving out the burnt gases in front of it.) The charge is then compressed by the piston and ignited at the dead

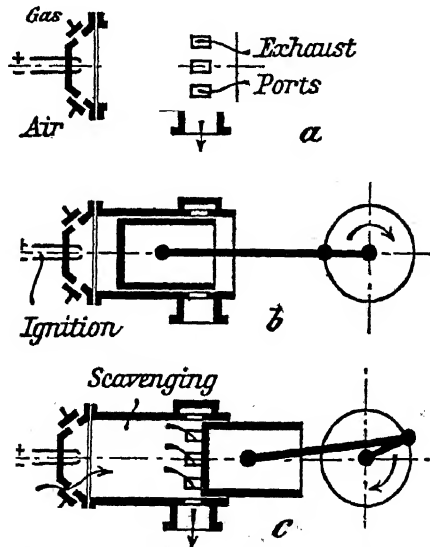


Fig. 48.—Diagram of a Two-stroke Engine

centre (or, on account of the finite duration of the explosion, a little before).

Double-acting Engines.—The two-stroke effect can also be attained in the case of four-stroke engines by arranging for the four-stroke

action to take place not only on one side of the piston, but (with corresponding displacement of the phases) on both sides. A similar combination of two-stroke processes gives a one-stroke engine, i.e. an engine which imparts an impulse to the crank-shaft every half revolution.

General.—The *ignition* is nowadays almost exclusively by means of electric sparks. The *duration* of the explosion is not very short; the following data, for instance, were obtained for coal gas at atmospheric pressure.

Volumes		Highest Pressure Produced (in atmospheres)	Duration of Explosion (in seconds)	Highest Temperature Produced (in °C.)
Gas	Air			
1	4	5.6	0.16	1600
1	6	6.3	0.04	1800
1	14	2.8	0.45	800

The greater the preliminary compression of the mixture, the more intense the explosion. Thus compression gives higher initial pressures and temperatures from the explosion and hence (as is easily seen from the work diagram whose area is a measure of the work done) an increased output of work (see p. 161). Hence the greater the compression of the charge before ignition, the higher the efficiency of an internal-combustion engine. A limit is set, however, by the heating effect of the compression. Naturally this must not be so great as to give rise to an explosion, otherwise the piston would receive an impulse when in an unfavourable position of its stroke—an event which might damage the engine ("knocking" in a motor).

Fuel.—Use may be made either of gases or of liquid fuels which may be gasefied in the engine. Besides coal gas, the gases most extensively used are those produced from the incomplete combustion of the various fuels by blowing in steam (suction gas, Mond gas, water gas, &c.), also blast-furnace gas and coke-oven gas. The chief liquid fuels are the light mineral oil distillates and also benzol and alcohol. They are brought into the form of spray in a carburettor by the suction of the air current flowing past a jet; this causes rapid evaporation and formation of the explosive mixture.

Diesel Engines (Constant-pressure Engines) (named after R. DIESEL *). These work on the same principle as other gas engines, but employ an extremely high compression (30–35 atm.). This causes a very great rise of temperature, such that all fuel mixtures would ignite spontaneously. The fuel is therefore sprayed in after the compression by means of a pressure pump. In consequence of the high

* RUDOLF DIESEL (1853–1913), engineer at Munich.

temperature the mixture explodes at once without any special ignition device. This method of working has considerable advantages which give greatly increased efficiency. Firstly, there is the high initial pressure, secondly, the great compression which makes the combustion very complete, and thirdly, the gradual addition of the fuel and the consequent slow combustion which delivers a fairly even pressure

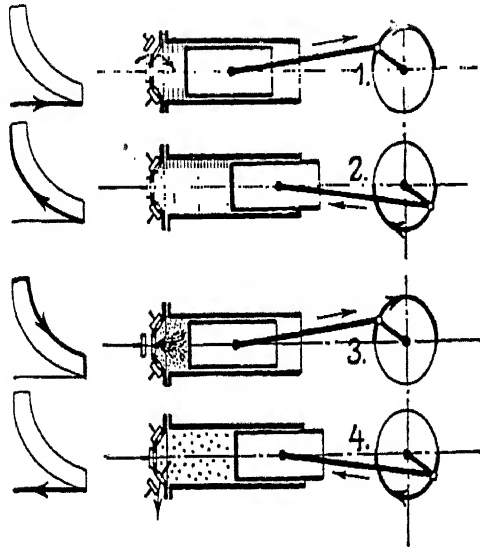


Fig. 49.—Diesel Principle

1, Suction. 2, Compression. 3, Working stroke. 4, Exhaust

over a period of time (constant-pressure engines). The difference between the Diesel engine and the ordinary type can be seen clearly from the respective work diagrams (figs. 49 and 45). A further advantage of using a very high temperature and spraying in the fuel is the possibility of using cheap, not easily vaporizable fuels, such as heavy oil and even tar. Experiments have also been carried out in which coal dust was made to explode in a Diesel engine; but so far no technical application of this has been possible. Diesel engines are built up to 2000 h.p. per cylinder.

CHAPTER V

Transference of Heat

1. Types of Heat Transfer

The passage of heat from one place to another can occur in three ways, by *convection*, *conduction*, and *radiation*.

1. **Convection.**—In *convection* the body carrying the heat also moves from the one place to the other. The propagation of heat in liquids and gases occurs chiefly in this manner, i.e. by simultaneous transport of matter. This can be seen in a beaker of water (fig. 1) heated from below with a small flame. Small suspended particles, e.g. sawdust or fragments of amber, rise directly above the flame and then sink again near the walls, thus maintaining a continuous circulation.

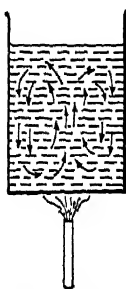


Fig. 1.—Convection in a Liquid

If a tube bent into the form of a rectangle (fig. 2) be filled with water and heated at one corner, the warm (and therefore specifically lighter) water rises up the corresponding vertical limb and sinks again in the opposite one. This can be seen well by adding a drop of dye solution or a trace of solid dye (e.g. methyl violet) through the upper opening during the heating, and then watching the movement of the coloured streaks. If the

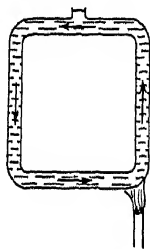


Fig. 2.—Diagram of Hot-water Heating System.

flame be removed from the one corner and placed under the other, the direction of flow of the water is reversed.

In a room the air currents due to heating can be made visible by means of tobacco smoke. This rises near the radiators and falls again near the windows. A lighted candle held at the chink of the door of a heated room shows the direction of flow of the air. Flames burning in still air are directed upwards because the burning gases and the air immediately next to them are hotter and therefore lighter than the surrounding atmosphere and hence rise upwards. The draught in lamp glasses and in chimneys is also caused by the rising of hot air, which simultaneously bears away the heat.

Convection plays a great part in winds and ocean currents. In the summer the east winds bring heat to central and western Europe from the hot parts of Russia; in winter they are cold and hold back the warm winds from the west. The Gulf Stream brings us heat from the tropics, thereby raising the mean temperature in west and central Europe about 10°C . above that of districts lying in the same latitudes on the east of North America and Asia (see Vol. V.)

On account of the presence of internal temperature differences in the substance convection is always accompanied by conduction of

heat (see below); in the case of large volumes of liquids and gases, however, this is small, and may be neglected in comparison with convection. The transference of heat by convection (plus conduction) depends upon the complicated laws of hydrodynamics governing the flow of liquids and gases.

The quantity Q cal. of heat transferred in this way can be represented mathematically by the expression

$$Q = \alpha' A \tau (t_1 - t_2),$$

where A is the area in cm.^2 , $(t_1 - t_2)^\circ \text{C.}$ the temperature difference concerned, and τ the time in seconds.

The factor α' gives the quantity of heat transferred per second through 1 cm.^2 of surface when the temperature difference is 1°C. In engineering it is referred to 1 m.^2 , 1 hour and the kilocalorie, and is then denoted by α . Its value varies very much with the conditions (roughness and shape of the boundary surfaces); but its value is known with sufficient accuracy for many technically important purposes. This type of heat transference decreases very rapidly in gases as the pressure is reduced (vacuum vessels, see p. 178).

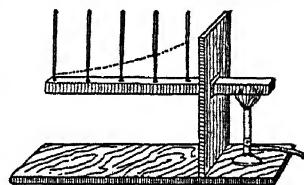


Fig. 3.—Temperature Gradient

2. Conduction of Heat.—In *conduction* the heat passes from the hotter to the colder part of a system without these parts moving relative to one another. Thus there is no transport of matter—only a transport of energy in consequence of the impacts of the molecules of the hotter part which have the higher energy. Thermal conductivity is therefore a property of matter. If one end of a needle is held in a flame, the other end becomes so hot after a minute or two that it cannot be held in the fingers without burning them.

Fig. 3 shows an arrangement in which a metal bar about 50 cm. in length and of 1 cm.^2 cross-sectional area is heated at one end by a flame. Thermometers inserted at equal intervals along the bar soon show rises of temperature. The nearer the thermometer to the heated end, the greater the temperature rise it indicates. The heat is propagated from the hot end along the bar to the other end by conduction. After a time the readings of the thermometers become constant; the curve in fig. 3 shows the different mercury levels in this steady state.

The process of conduction may be imagined to consist of continual equalization of the temperatures of every pair of neighbouring elements of the bar. If this were the only process, the whole of the bar would soon take up the same temperature, namely, that of the heated end. But heat is being removed simultaneously from the surface of the bar by the surrounding air. Thus the bar is being cooled at all points except at the heated end; and the rate of cooling is greatest where the temperature difference relative to the air is greatest (see p. 179).

Hence the temperature of the bar at any given point is determined by the rate of gain of heat from the warmer side and by the rate of loss of heat both to the colder side and to the surrounding air. The stationary state is reached when these rates are equal at all points of the bar.

In the above experiment we have to consider two factors; firstly, the **conduction** of the heat within the rod, and secondly, the loss of heat to the surroundings, mainly by convection.

The (*internal*) *conduction* depends only upon the nature of the substance used, i.e. is a specific property of that substance. In order to define this more exactly, imagine two large vessels separated by a large plate of the substance 1 cm. thick. The vessels are filled with a liquid so that there is a temperature difference of 1°C. between them. Then a certain quantity of heat passes per second through each square centimetre of the conducting plate.

The quantity of heat, expressed in gramme-calories, which passes per second through a cross-section of 1 cm.^2 of a plate 1 cm. in thickness with a temperature difference of 1°C. between its faces, is called the specific thermal conductivity k of the substance.

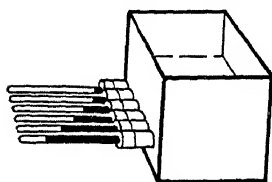


Fig. 4.—Ingenhousz's Experiment upon Thermal Conductivity. Rods of Copper, Brass, Zinc, Iron, Lead, Glass (in order of nearness).

Its dimensions are therefore [$\text{cal. degree}^{-1}\text{ cm.}^{-1}\text{ sec.}^{-1}$]. The engineering value, which is referred to the kilocalorie, metre and hour, is 360 times larger. The thermal conductivity k is different for different substances: for silver, 1.01; copper 0.9; iron 0.15; lead 0.08; glass, 0.002 $\text{cal. degree}^{-1}\text{ cm.}^{-1}\text{ sec.}^{-1}$ (see also Table I).

In 1822 FOURIER first developed the mathematical laws of thermal conductivity in a purely empirical manner and without recourse to molecular theory. In a body not at uniform temperature the conduction of heat takes place in the direction of the normals to the isothermal surfaces, i.e. the surfaces of equal temperature within the body. On the simplifying assumption that these surfaces are parallel planes and that the heat only flows in the x -direction, the quantity Q of heat transferred by conduction is given by the equation

$$Q = kA\tau \frac{dt}{dx},$$

where t is the temperature, τ the time, A the area, $\frac{dt}{dx}$ the temperature gradient, and k the thermal conductivity.

The difference of the thermal conductivity of solids can be observed by holding a rod of copper about 6 cm. long and 2 mm. diameter in one hand and a similar rod of iron in the other, and placing the opposite ends in the same flame. It will be noticed that the copper rod gets hot much sooner than the iron one. Similarly one end of a glass rod may be held in the hand while the other is heated to white heat and melted; but an iron rod becomes so hot before its end is red hot that it can no longer be held in the hand.

The same thing can be demonstrated by means of INGENHOUSZ's trough (fig. 4). In this similar rods of different materials are inserted through the wall of the same trough so as to project equal distances from it. The rods are coated either with wax or with the double iodide of silver and mercury. When the trough

is filled with hot water, the different conducting powers of the various materials can be seen at once from the fact that the wax melts to different distances or the double (which at ordinary temperature is light yellow, but changes almost suddenly to orange at $35^{\circ}\text{C}.$), changes its colour to different distances along the different rods.

Vessels for hot liquids are usually provided with wooden handles, so that they may be grasped without burning the hand. In the DAVY miner's safety lamp (fig. 5) a wire gauze surrounding the flame keeps the temperature of the gases leaving the lamp below the ignition temperature of the combustible gases which might be present in the atmosphere of the coal mine, thus preventing explosion.

Such metal gauzes are also used in petrol containers (e.g. in motor-car carburettors) as a safety device against the propagation of an explosion in the interior.

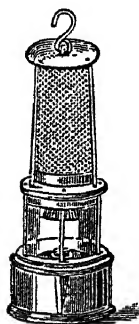


Fig. 5.—Davy Safety Lamp

The thermal conductivity of crystals is different in different directions. If a plate cut out of a gypsum crystal be covered with wax and a wire passed through a hole in the middle of it, the wax does not in general melt in a circle around the wire when the latter is

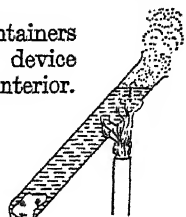


Fig. 6.—Experiment illustrating the Small Thermal Conductivity of Water.

heated, but in an ellipse (according to the direction of the section).

The thermal conductivity of liquids is very small in comparison with that of metals. In investigating the thermal conductivity of liquids care must be taken to exclude transference of heat by convection. Fig. 6 depicts an experiment upon a test-tubeful of water at the bottom of which is a small piece of ice loaded with lead. By heating the water at the top of the tube with a flame it can be boiled without melting the ice below.

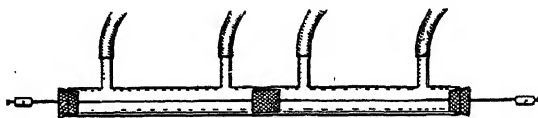


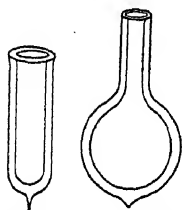
Fig. 7.—Thermal Conductivity of Gases

The thermal conductivity of gases is still smaller. This is the reason why loose fabrics, peat-fibre or straw protect hot or cold bodies against change of temperature (woollen clothes, beds, double windows, fireless cooker). The hollow walls of icehouses are filled with peat-mould and straw. The individual pieces of the filling minimize convection so that only the thermal conductivity of the air contained in the wall is effective. The thermal conductivity of water is about $1/600$, that of air about $1/20,000$. (See pp. 183, 184.)

The thermal conductivity of different gases varies considerably. It is relatively great in the case of hydrogen, namely 7 times as great as for air. These differences may be demonstrated with the apparatus shown in fig. 7. This consists of a glass tube with a stopper in the middle and at each end. Through these

stoppers pass copper rods holding two similar pieces of platinum wire, one in each compartment of the tube. These wires are heated electrically and both glow with equal intensity when both compartments are filled with the same gas. If, however, different gases be introduced or one compartment evacuated by means of the side tubes, the intensity of the glow is altered. It is brightest in vacuo, because there is no gas and consequently no thermal conductivity; it is less bright in carbon dioxide, still less in air. If one half of the tube be filled with hydrogen and the other with air, the platinum in the former will hardly glow when that in the latter is at a bright red heat.

The Leidenfrost phenomenon (also known as the *spheroidal state*) depends upon the poor thermal conductivity of water vapour. When drops of water are sprinkled upon a clean red-hot metal dish, they move about upon the surface without boiling. The explanation of this lies in the fact that the extremely rapid vaporization between the drops and the red-hot dish gives rise to a thin layer of steam. The drops are borne upon this cushion and thus protected against rapid heating by its poor thermal conductivity. The temperature of the water drops in the spheroidal state is about 97°C .



Figs. 8 and 9.—Dewar Flasks

An effective method of protecting vessels against loss or gain of heat is to provide them with double walls and to evacuate the space between (vacuum-walled vessels or Dewar flasks (figs. 8 and 9)). Vessels of this type were first made in 1881 by WEINHOLD at Chemnitz. DEWAR* later (1890) introduced a great improvement by silvering them on the inside. This also reduces loss and gain of heat by radiation. Liquid air can be kept for days in silvered Dewar flasks. The so-called *thermos-flasks* for keeping drinks or food hot or cold for considerable periods are Dewar flasks enclosed in sheet-metal cases to protect them against mechanical damage.

3. Heat Radiation.—In *radiation* the passage of heat from one body to another takes place without the agency of matter. The sun sends us its warming rays without causing any rise of temperature in the space between. On cold winter days, when the air temperature is below the freezing-point of water, a thermometer exposed to direct sunlight (especially if its bulb is blackened) will register considerably over 0°C .

Thermal conductivity and convection involve the agency of matter, the heat energy passing from a place of higher temperature to one of lower temperature in the form of molecular motion; but in heat radiation the only agent is the ether. The thermal energy must first change into another form, namely, into electromagnetic waves. Hence heat radiation cannot be discussed until Vol. V. In most cases it consists mainly of a kind of invisible light (infra-red radiation).

We know that some substances are more and some less transparent for visible light; the same is also true for heat radiation. Substances which are transparent to heat radiation are said to be *diathermic* or *diathermanous*, those which are opaque to heat radiation are *adiathermic*.† These properties do not run parallel with ordinary transparency and opacity. Thus glass, for example, is very adiabthermic,

* JAMES DEWAR (1842–1923), Professor at Cambridge. Vacuum-walled vessels are usually called DEWAR flasks.

† Gr., *a*, not; *dia*, through; *thermē*, heat.

Upon this depends the action of greenhouses. The visible rays of the sun pass through the glass without being appreciably weakened. They thus warm up the bodies in the greenhouse. The heat radiation emitted by these bodies cannot get out again, however, because the glass is opaque to it (*greenhouse principle*).

4. Law of Cooling.—When a hot body is left in the air, it gradually becomes colder owing to loss of heat (mainly by convection and radiation) to its surroundings. The greater the temperature difference, the more rapid the loss of heat, the rate of cooling being directly proportional (within certain limits) to the temperature difference and to the time (**Newton's law of cooling**). The velocity of cooling is the quotient of the temperature fall divided by the time. The quantity of heat lost from unit of area of a surface, per unit time and per unit excess of temperature over that of the surrounding medium, is called the **emissivity** of the surface with respect to that medium.

If T is the temperature of the body, T_1 that of the surroundings, and t the time, then

$$\frac{dT}{dt} = -K(T - T_1).$$

Hence

$$\frac{dT}{T - T_1} = -K dt$$

and by integration $\log_e(T - T_1) = -Kt + \text{const.}$

If at the time $t = 0$ the initial temperature was T_0 , then the integration constant is equal to $\log_e(T_0 - T_1)$. Hence we have

$$\log_e(T - T_1) - \log_e(T_0 - T_1) = -Kt$$

or

$$T = T_1 + (T_0 - T_1)e^{-Kt}.$$

The constant K depends upon the mass, the specific heat and the nature of the surface of the body. The above equation shows that the temperature at any moment can be calculated, provided that the initial temperature of the body and the value of the constant K be known. The latter must be obtained by preliminary experiments. The equation is of general importance in so far as it states that:

When the rate of change of the state of a body is proportional to the difference between that state and a constant reference state, then the state of the body is determined by an exponential function of the time.

2. Experimental Methods of Determining Thermal Conductivity

The methods used to determine thermal conductivities vary greatly with the nature of the substance under investigation. Four cases may be distinguished: (A) solids which are good conductors (metals); (B) solids which are moderate or poor conductors (woods, sand, stones, bricks, cork, charcoal); (C) liquids; (D) gases.

A. Good Conductors (metals).—For these, a rod or bar is nearly always used. We shall describe (i) a direct method, (ii) an electrical method, (iii) a comparative method.

(i) *Direct Method*.—The earliest direct determination of the conductivity of a metal was that of Forbes.* His method was of no great accuracy, but has been much improved by Callendar and others. One end of the bar is heated, the other end cooled. The heating may be done electrically, and the cooling by means of a stream of water. The heat passing into the water can be found from the rate of flow and the rise of temperature; the heat supplied at the other end is determined electrically. The temperature at various points of the bar is found by means of thermo-couples, and the temperature gradient deduced. The heat flowing across any section of the bar is determined as the sum of the heat flowing into the water and the heat lost from the surface between the section and the cold end; as a check, this sum ought to be equal to the heat supplied, less the heat lost between the section and the hot end. The losses from the surface can be made small by lagging, so that the temperature gradient is practically uniform; and the actual values of the losses can then be measured approximately, by heating the whole bar to a uniform temperature, and recording the rate of cooling.

From the observed flow of heat and temperature gradient, the value of k follows at once from its definition.

(ii) *Electrical Method*.—A good method of determining the thermal conductivity of a metal is to observe the distribution of temperature in a rod of the metal when it is heated by an electric current. The method was originally suggested by Kohlrausch, and was applied in an important series of experiments (1899) by Jaeger and Diesselhorst.

The principle underlying the method is simply this, that the heat generated in any element of the rod, when the steady state has been reached, is equal to the heat which leaves the element by conduction, assuming that there is no loss of heat from the sides. We may suppose that the flow, both of electricity and of heat, takes place in lines parallel to the axis. Consider a section P at distance x from one end, and let v , T be the electric potential and temperature at P. Similarly, let $v + dv$, $T + dT$ be the corresponding values for the section Q at distance $x + dx$. Let A be the cross-section, k the thermal conductivity, and σ the electrical conductivity. We shall suppose that k and σ are both independent of the temperature.

The heat entering the element at P is

$$-kA \frac{dT}{dx},$$

and the heat leaving at Q is

$$-kA \frac{dT}{dx} - \frac{d}{dx} \left(kA \frac{dT}{dx} \right) dx.$$

The gain per unit time from conduction is therefore

$$kA \frac{d^2T}{dx^2} dx.$$

*JAMES DAVID FORBES (1809–68), Professor of Natural Philosophy in the University of Edinburgh (1833–60), afterwards Principal of the University of St. Andrews.

The gain of electrical energy by the element per unit time is equal to the square of the potential difference between P and Q divided by the resistance of the element, or, if m is a coefficient depending on the units used, the gain is

$$m \left(\frac{dv}{dx} \right)^2 \cdot A \sigma / dx,$$

or
$$mA \sigma \left(\frac{dv}{dx} \right)^2 dx.$$

Hence
$$k \frac{d^2 T}{dx^2} + m \sigma \left(\frac{dv}{dx} \right)^2 = 0. \quad \dots \dots \dots (1)$$

But we may regard T as a function of v , so that

$$\begin{aligned} \frac{dT}{dx} &= \frac{dT}{dv} \frac{dv}{dx}, \\ \frac{d^2 T}{dx^2} &= \frac{d^2 T}{dv^2} \left(\frac{dv}{dx} \right)^2 + \frac{dT}{dv} \frac{d^2 v}{dx^2}. \quad \dots \dots \dots (2) \end{aligned}$$

Now the current is constant, and therefore dv/dx is constant, and $d^2 v/dx^2 = 0$. Thus, from (1) and (2),

$$k \frac{d^2 T}{dv^2} + m \sigma = 0,$$

and, by integration,

$$\frac{k}{m \sigma} T = -\frac{1}{2} v^2 + Cv + D,$$

where C and D are constants.

Hence, by observing T and v at three points, we can determine C and D , and then k/σ . If σ be known independently, this gives k .

(iii) *Comparative Method.*—The conductivity of a metal may often be conveniently determined by comparison with another metal whose conductivity is known.

The method depends on the law of the steady flow of heat along a bar, one end of which is kept at constant temperature, while its length is subjected to radiation and convection inside an enclosure the temperature of which is also constant.

In the notation just used for the electrical method, we prove as before that the section between x and $x + dx$ gains per unit time from conduction the quantity of heat

$$kA \frac{d^2 T}{dx^2} dx.$$

It loses from the surface of the element the quantity

$$E p T dx,$$

where E is the emissivity and p is the perimeter of the section (p. 179). Hence, in the steady state

$$\frac{d^2 T}{dx^2} = \frac{E p}{k A} T.$$

The solution of this differential equation is

$$T = Ce^{nx} + De^{-nx},$$

where $n = \sqrt{(Ep/kA)}$, and C, D are arbitrary constants. Suppose now that the temperatures at three points, equally spaced at distances $x + a, x, x - a$, say, are T_1, T_2, T_3 . Then it is easily verified that

$$\frac{T_1 + T_3}{2T_2} = \frac{e^{na} + e^{-na}}{2}.$$

If $(T_1 + T_3)/2T_2$ is known, and has the value r , this equation is a quadratic to find e^{na} , and gives

$$na = \log_e(r + \sqrt{r^2 - 1}).$$

It follows that if we take two bars of different metals, but having the same cross-section A , perimeter p , and emissivity E , and observe the temperatures in both at three equally spaced points at the same distance apart, we get the ratio of the conductivities from the equation

$$\sqrt{\left(\frac{k}{k'}\right)} = \frac{\log(r' + \sqrt{r'^2 - 1})}{\log(r + \sqrt{r^2 - 1})}.$$

This method was used in 1854 by WIEDEMANN and FRANZ. They secured equal emissivities by electroplating their rods. Since, however, Newton's law of cooling is only true for small temperature differences, the method is not very accurate.

B. Solid Non-metals.—The conductivity of small thin slabs of material has been determined by Lees by a method which is applicable over a wide range of temperatures. The arrangement is shown in fig. 10.

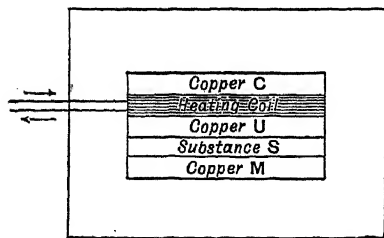


Fig. 10

The substance S was contained between two copper blocks or discs U and M , and the heating coil between U and a third copper block C . The thicknesses were: U and M , 3 mm.; C , 1 mm. The temperatures of all the copper blocks were measured by thermo-couples.

When the discs had been assembled they were varnished to give them the same emissivity (p. 179), and the whole apparatus was suspended in an enclosure of constant temperature.

In the theory given below, the following symbols are used:

H = rate of supply of energy to the heating coil, after the steady state has been reached.

h = heat loss per second per sq. cm. for 1° excess of temperature of discs over that of enclosure.

t = excess of temperature over that of enclosure.

d = thickness of disc.

r = radius of disc.

The heat received per second by the disc M and given up to the air is

$$(\pi r^2 + 2\pi r d_M) h t_M.$$

The heat received per second by S and given up to the air from its exposed surface or passed on to M is

$$(\pi r^2 + 2\pi r d_M) h t_M + 2\pi r d_S h \cdot \frac{1}{2}(t_M + t_U).$$

If k is the thermal conductivity of the disc S, the heat flowing through it is

$$\pi r^2 k \frac{t_U - t_M}{d_S}.$$

We may assume that the heat flowing through S is the mean of the quantities of heat flowing into it and out of it, i.e. that the third of the above quantities is half the sum of the other two. We have, therefore, on dividing by πr^2 ,

$$k \frac{t_U - t_M}{d_S} = h \left[t_M + \frac{2}{r} (d_M + \frac{1}{2} d_S) t_M + \frac{1}{2r} d_S t_U \right].$$

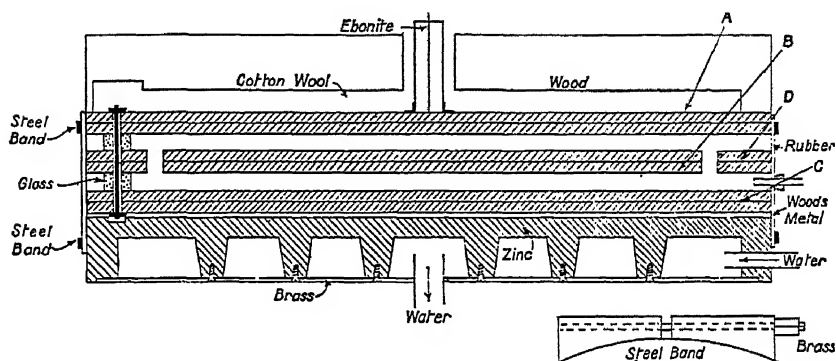


Fig. 11

This gives k in terms of h and measured quantities. But we can obtain h in terms of H , since the total heat supplied must be equal to that given up by the various surfaces. Thus

$$H = \pi r^2 h (t_U + t_M) + 2\pi r h \{d_M t_M + d_S \cdot \frac{1}{2}(t_M + t_U) + d_U t_U + d_C t_C\}.$$

We can therefore express k in terms of quantities that can be measured.

C. Liquids.—The determination of the conductivity of a liquid is complicated by the fact that convection currents are very easily set up in a liquid in which there is a temperature gradient. The commonest way of overcoming this difficulty is to eliminate convection by supplying heat at a horizontal surface at the top of the liquid, and abstracting heat at a similar surface at the bottom (p. 177).

The conductivities of many liquids were determined by Lees in this way. He followed a somewhat similar method to that just described for non-metallic solids, but the disc of the substance S (fig. 10) was replaced by a film of liquid about 1.2 mm. thick, filling the space between the copper discs M and U, and contained within an ebonite ring of slightly greater diameter than that of the discs. The flow through the ebonite was found by an independent experiment, with air occupying the place of the liquid.

D. Gases.—In gases it is necessary to guard against, or take account of, the disturbing effects both of convection and of radiation. One satisfactory method is that of Hercus and Laby. Their apparatus is shown in fig. 11.

All the plates were of copper. The air experimented on was contained between the hot plate B and the water-cooled plate C. The plate A was kept at the same temperature as B, and so prevented any loss of heat from the upper surface of B. B was surrounded by a guard ring D, which was maintained at the temperature of B by an auxiliary heating coil. The heating of B was effected by a heating coil between the two plates, clamped together, of which B consisted. All the heat generated in B flowed to C, and the heat flow was therefore determined by measuring the electrical energy supplied to the heating coil in B. The temperatures of all the copper blocks were measured at various points by attaching constantan wires to them, these forming thermo-couples with the blocks, each of which had a copper lead attached to it.

Since the heat flow is all downwards, there is no convection in this method, but radiation has to be allowed for. In Hercus and Laby's experiments, the correction for radiation amounted to about 5 per cent of the whole transfer of heat. It was determined by separate experiments on the loss of heat from a silvered Dewar flask.

APPENDIX

SOME EXPERIMENTAL METHODS

JOULE'S EQUIVALENT. SPECIFIC HEAT

1. Continuous-flow Calorimetry

Some of the best determinations of specific heats, both of liquids and of gases, have been carried out by the method of continuous-flow calorimetry. This is a method which was developed by CALLENDAR and BARNES for the purpose of obtaining the value of the mechanical equivalent of heat. As a by-product of their research, these physicists made a very accurate determination of the specific heat of water over a wide range of temperatures. An account of their methods and results will now be given (§§ 2, 3).

2. Joule's Equivalent

The steady-flow electric calorimeter, which was the instrument used by Callendar and Barnes, is shown diagrammatically in fig. 1.

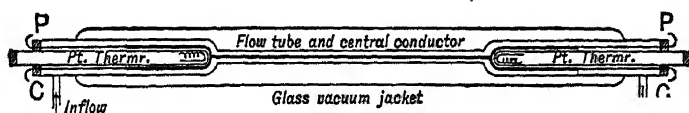


Fig. 1

A steady current of water flowed through the central tube. The water was heated by a steady electric current in a conductor of platinum. When the difference of temperature between the inflowing and the outflowing water had become steady, it was measured by means of a differential pair of platinum thermometers at the two ends. The bulbs of the thermometers were surrounded by thick copper tubes, which served the double purpose of equalizing the temperature, and of preventing the current from generating heat immediately beside the thermometer bulbs. The current was introduced by the leads CC. The difference of potential on the central conductor was measured by the leads PP, which were carefully insulated. The flow tube was of glass, and was sealed at each end, beyond the thermometer bulbs, into a glass vacuum jacket, which helped to diminish the loss of heat

to the outside. The whole apparatus was enclosed in a copper jacket (not shown in the figure). Water circulated rapidly in the jacket, and was kept at a constant temperature by a very delicate electric regulator.

The equation on which the method depends may be written

$$ECt = JM \, dT + H.$$

In this equation E is the difference of potential on the central conductor, and C is the current. These were both measured with great accuracy by means of a carefully calibrated potentiometer. M is the mass of water flowing in time t ; dT is the rise of temperature, and H the loss of heat in joules, also for time t . J is the mechanical equivalent of heat, or, more definitely, the number of joules in 1 calorie at a temperature which is a mean of the range dT .

The time of flow t was generally about 15 to 20 min., and was recorded automatically. M was usually about 500 gm., and dT from 8 to 10 degrees. The thermometer readings were considered to be correct to one-thousandth of a degree. The loss of heat to the outside, H , was small and could be estimated and eliminated.

Callendar and Barnes laid great stress on the necessity for absolute steadiness in all the conditions. By attending to this, it becomes unnecessary to take account of the thermal capacities of the various parts of the apparatus, which otherwise would be very troublesome.

They also pointed out the importance of having the water well mixed on its way along the tube; and to meet this requirement used a stranded conductor for heating.

In the equation

$$ECt = JM \, dT,$$

E and C , which were measured in volts and amperes, can be reduced to electromagnetic units, and ECt can thus be expressed in ergs.

The above equation can therefore be interpreted as giving the value of the mechanical equivalent of the calorie from the measurement of the electrical energy required to produce a measured amount of heat.

3. Specific Heat of Water

But, apart from giving the value of J , these experiments of Callendar and Barnes also determine how far the specific heat of water depends on the temperature. For this application it is not essential that the absolute values of the electric standards should be known, since only relative amounts of energy at different temperatures are here in question.

The following table shows the values obtained by Callendar and Barnes for the specific heat of water at various temperatures.

Temperature (°C.)	Specific Heat of Water
5	1.0047
10	1.0019
15	1.0000
20	0.9988
25	0.9980
30	0.9976
35	0.9973
40	0.9973
45	0.9975
50	0.9978
60	0.9987
70	1.0000
80	1.0017
90	1.0036
100	1.0057

4. The Two Specific Heats of a Gas

Constant Pressure.—The method of continuous flow, or steady electric heating, used by Callendar and Barnes in the research just described, was first applied to gases by Swann. The most accurate work using this method is that of Scheel and Heuse, who dealt with temperatures between -180° C. and room temperature.

Their calorimeter was of glass, and sealed within an evacuated tube so as to avoid heat loss. The whole calorimeter was immersed in a constant-temperature bath. After passing through a long tube immersed in this bath, the gas entered the calorimeter at the bottom, and flowed past a platinum thermometer, which measured the inlet temperature. The heater was of constantan wire. To reach it the gas had to follow a devious path, where it intercepted any heat escaping from the heater. A second platinum thermometer measured the temperature of the outgoing stream.

The total mass of gas passing through the instrument, and the rise of temperature, are known, as well as the heat electrically supplied; the specific heat can therefore be calculated at once, as in the method of Callendar and Barnes.

Constant Volume. The Joly Steam Calorimeter.—The specific heat of gases at constant volume was first accurately determined by Joly, in 1890. The steam calorimeter which he used is shown in fig. 2. A front view is shown on the left, and a side view on the right. Two equal copper spheres, one exhausted and the other containing the gas, hang from the two arms of a balance in a closed chamber. When

temperature equilibrium is established, steam is admitted. The steam condenses on the spheres, which are thus raised to the temperature of the steam. Pans are provided to catch the water so condensed. More water is condensed on the full sphere than on the empty one, and the difference is measured by adding weights to restore the balance. This difference, multiplied by the latent heat of vaporization of water, gives the heat required to raise the known mass of gas in the full sphere

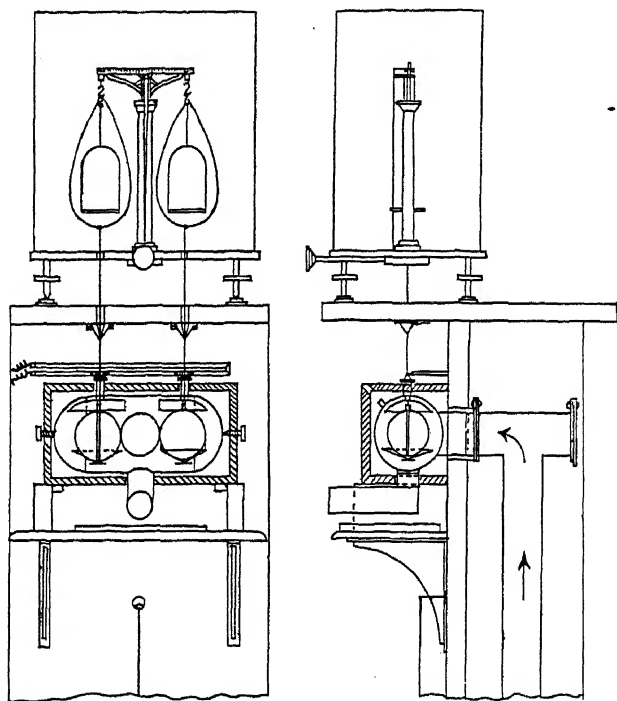


Fig. 2

from its initial temperature to that of the steam. The specific heat of the gas at constant volume can then be calculated at once.

Corrections are necessary for:

(a) Expansion of the heated sphere and consequent work done by the gas.

(b) Increase of volume of the full sphere under the increased pressure of the gas.

(c) Buoyancy effects due to difference in the expansions of the spheres.

(d) Unequal thermal capacities of the spheres.

(e) Reduction of weight of precipitated water to weight in a vacuum.

VIBRATIONS AND WAVES

CHAPTER I

Vibrations

1. General Treatment of Vibrations

1. When a system is slightly displaced out of its condition of stable equilibrium, it will in general tend to return to it. But the original equilibrium condition is hardly ever reached by a single reversal of the displacement; the condition of the system usually overshoots this mean and then oscillates or *vibrates* about it until the vibrations are stopped by external forces.

The time between two successive passages in the same sense through the equilibrium condition is called the *period* of the vibration.

The number of complete vibrations, or *cycles*, per unit of time is called the **frequency**. It is measured in cycles per second, and therefore has the dimension $[\text{sec.}^{-1}]$. The unit of frequency, i.e. 1 cycle per second, is sometimes called the **hertz**.*

A simple example of such a system is the *pendulum* already treated at p. 144, Vol. I. The equilibrium position is vertically beneath the point of suspension (position of rest). The period of a simple pendulum (Vol. I) is $T = 2\pi\sqrt{l/g}$ and that of a compound pendulum $T = 2\pi\sqrt{I/R_1}$. Another example already treated is torsional vibration (p. 207, Vol. I).

Further Examples.—*Longitudinal elastic vibrations.* A long thin metal wire is fastened at one end to the ceiling and the other end is loaded with a mass m . This stretches the wire and enables the mass to perform vibrations by virtue of the elastic forces. In order to calculate the period of these vibrations, the wire is loaded with an extra weight sufficient to extend it 1 cm. further; or alternatively the extra extension caused by a known added load is measured and the magnitude of the force required to produce an extra extension of 1 cm. is obtained by calculation. This force, expressed in dynes, is the quantity k in the general

* In honour of H. HERTZ, who was the first physicist to demonstrate by experiment the existence of electric waves.

formula for the period of a vibration (p. 148, Vol. I). The mass m being known (in gm.), the period T can be calculated from the equation

$$T = 2\pi\sqrt{\frac{m}{k}}.$$

Conversely the force k may be calculated from the observed period of vibration and known mass, and the value so obtained used for the determination of the modulus of elasticity of the wire.

The same experiments can also be carried out very conveniently with a spiral spring. In this case the elongation is not produced by extension of the wire but by bending and twisting of the coils.

Vibrations of a Liquid in a U-Tube.—If the cross-sectional area of the U-tube is a , the density of the liquid s , and the total length of the liquid column l , the mass of the liquid in the tube is $m = las$. If now the liquid be raised 1 cm. in one limb (say by sucking at the end), it falls by 1 cm. in the other. The level in the first limb is therefore 2 cm. higher than in the second. The weight of the excess column, expressed in dynes, is the force k , hence $k = 2asg$. The period of vibration is therefore

$$T = 2\pi\sqrt{\frac{las}{2asg}} = 2\pi\sqrt{\frac{l}{2g}}.$$

The period is thus independent of the cross-section of the tube and the density of the liquid. It is the same as the period of a pendulum whose length is half that of the liquid column. For the practical application of such vibrations in the anti-rolling tank see p. 202.

2. Graphical Representation of Vibrations.—This may be illus-

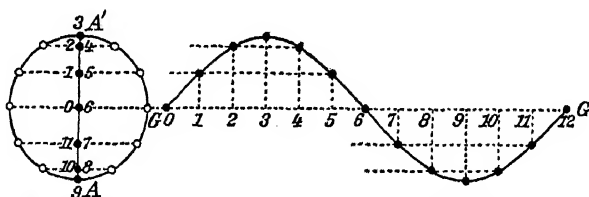


Fig. 1.—Time-Displacement Curve for a Simple Harmonic Vibration

trated for the case of harmonic motion (Vol. I, p. 146). This can be regarded as the projection of a uniform circular motion upon a diameter. This circular motion and its projection upon the diameter AA' are represented in fig. 1. The times are plotted as abscissæ along a horizontal straight line GG' , the ordinates being the corresponding displacements of the vibrating point. The graph so obtained is a *sine curve*. Instead of the time, the *phase* (which is proportional to the time, Vol. I, p. 146) may be chosen as abscissa. This representation, which is generally preferable, is employed in fig. 2, which shows the displacement x (as in fig. 1) and also the magnitude of the velocity u and acceleration a at each instant. Since in harmonic motion the displacement, velocity and acceleration are proportional to the sine (or cosine) of the phase, this kind of vibration is often called *sine vibration*.

The experimental proof that the swings of a pendulum follow the sine law for small amplitudes can be obtained as follows. The pendulum, which consists of a heavy funnel-shaped vessel with an opening at its point, is suspended as in fig. 3.

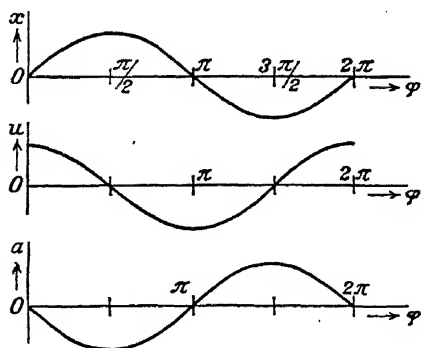


Fig. 2.—The Displacement, Velocity and Acceleration in Simple Harmonic Motion as a Function of the Phase

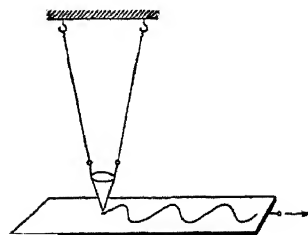


Fig. 3.—Tracing of Pendulum Vibrations

It is filled with sand and set swinging while a plane board is pulled along underneath it with uniform velocity in a direction at right angles to the plane of swing. The sand running out of the funnel traces a sine curve as the graph of the displacement-time law.

If a narrow glass trough be placed underneath the funnel and parallel to the direction of swing (fig. 4), the sand is piled up most where the pendulum moves slowest, the depth being inversely proportional to the velocity of swing. The curve of the surface of the sand in the trough is found to be such that the depth is inversely proportional to the cosine of the phase.

3. Damped Vibrations.—Observation shows that all vibrations, unless they are continually excited afresh, gradually decrease in amplitude and die out until finally the stable position of rest is reached. Such vibrations are said to be **damped**. The decrease of amplitude is due to the action of forces resisting the motion of the system, e.g. friction of

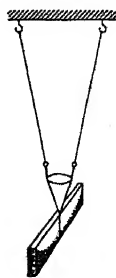


Fig. 4.

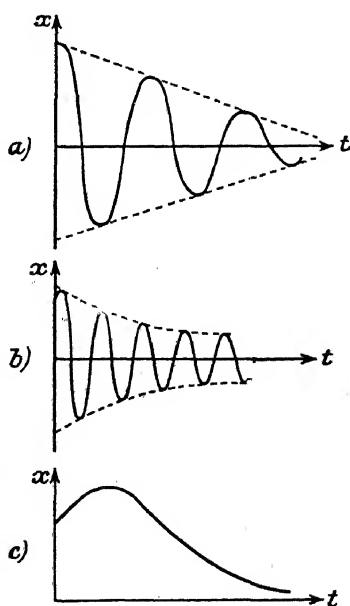


Fig. 5.—Damped Vibrations

bearings, air resistance and the like. The amplitude may decrease in various ways; either in *arithmetical progression* (fig. 5a), as, for example, in certain cases where the friction is constant; or in

geometrical progression (fig. 5b), when the opposing force is always proportional to the rate of increase of some co-ordinate (e.g. like air resistance, proportional to the velocity of a moving body). This latter case of a geometrical decrease of amplitude is especially common and important. When the damping is so great that the amplitude becomes zero after one or even half a period (fig. 5c), the motion is said to be *aperiodic*. If the successive amplitudes in the case of geometrical decrease are a_1, a_2, \dots, a_n , then

$$\frac{a_1}{a_2} = \frac{a_2}{a_3} = \frac{a_n}{a_{n+1}} = k.$$

The constant k , the damping factor, is a measure of the damping. Frequent use is also made of $\Lambda = \log_e k$, the *logarithmic decrement*.

The period T of a damped vibration is greater than that (τ) of the undamped vibration. The two are connected by the equation

$$T = \tau \sqrt{1 + \frac{\Lambda^2}{\pi^2}}.$$

This result may be proved as follows:

The equation of an undamped simple harmonic vibration (Vol. I, p. 146) is

$$\ddot{x} + n^2x = 0,$$

the solution of which is

$$x = A \sin(\pi t - \alpha),$$

where A and α are constants, and the period is

$$\tau = \frac{2\pi}{n}.$$

The corresponding damped vibration is given by the equation:

$$\ddot{x} + 2a\dot{x} + n^2x = 0,$$

which has for solution

$$x = Be^{-at} \sin(\sqrt{n^2 - a^2}t - \beta),$$

as may easily be verified by differentiation and substitution.

The period is now

$$T = \frac{2\pi}{\sqrt{n^2 - a^2}}.$$

After each half period the amplitude is diminished in the ratio $e^{-iat} : 1$.

Hence

$$k = e^{iat},$$

and

$$\Lambda = \frac{1}{2}aT.$$

Thus

$$T^2(n^2 - a^2) = 4\pi^2,$$

or

$$T^2 \left(\frac{4\pi^2}{\tau^2} - \frac{4\Lambda^2}{T^2} \right) = 4\pi^2,$$

which gives

$$\frac{T^2}{\tau^2} = 1 + \frac{\Lambda^2}{\pi^2}.$$

2. Combination of Vibrations

When a body performs two vibrations simultaneously, the resultant motion may be found by the parallelogram law. It is necessary here to distinguish between two cases: (1) where the directions of the partial vibrations coincide and (2) where they are at right angles to one another. All other cases can be referred back to these two.

1. **The Directions of the Partial Vibrations are Coincident.**—The resultant displacement is obtained by the algebraic addition of the displacements of the partial vibrations.

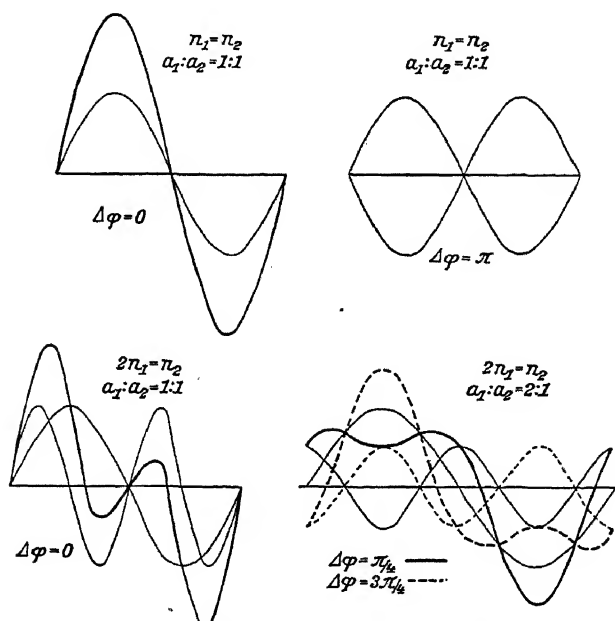


Fig. 6.—Composition of Two Vibrations of Different Frequency n , Amplitude a and Phase ϕ in the same Direction

Fig. 6 gives examples of such combined curves. Special interest attaches to the case of the *mutual neutralization of two vibrations with equal frequency and equal amplitude, but with a phase difference of π ($= 180^\circ$)*. This special case is of great importance, particularly in optics.

The combination of two harmonic vibrations can be carried out conveniently with the help of the apparatus shown in fig. 7. This consists of a strong frame of four vertical rods connected together at their upper ends by a frame. This frame carries an easily rotating horizontal axis, from which hang two rods loaded at their lower ends with cylinders of brass. These are connected together by four strong short rods, and between them is stretched a steel wire to which a vertical cross rod is attached at its middle point. Upon this rod slide four adjustable weights.

The vertical rod carrying the sliding weights can perform torsional vibrations about the steel wire as axis. In addition the whole suspended system can swing as a pendulum. These two types of vibrations are independent of one another.

The period of the loaded rod can be varied within wide limits by sliding the adjustable weights. When the pendulum and also the rod are set swinging the lower end of the latter performs both vibrations simultaneously. It is provided with an adjustable thin glass point, which traces out the vibrations upon a glass

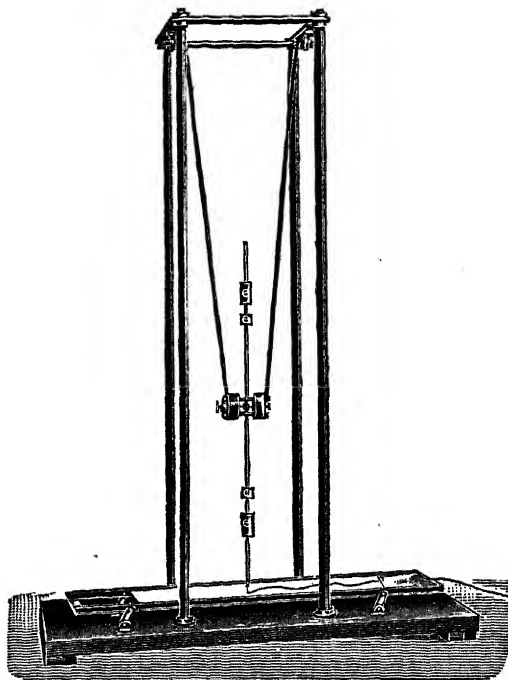


Fig. 7.—Grimsehl's Apparatus for tracing Two Superimposed Vibrations

plate covered with dust. The plate being at rest, the trace is a single straight line; but when the plate is pulled with uniform velocity along the straight rails at right angles to the direction of swing, a curve is obtained which represents the sum of the two vibrations.

The case of the superposition of two vibrations of almost equal frequency is of special interest. The addition gives a resultant vibration of somewhat variable period (fig. 8) and, what is more important, of regularly variable amplitude. These variations of amplitude or **beats**, as they are called, themselves have a frequency which is equal to the difference between the frequencies of the two component vibrations.

Example.—When two vibrations with frequencies of 30 and 31 per second interfere, the resultant amplitude reaches its maximum once every second; the beat frequency is therefore 1 per second. When frequencies of 30 and 32 per second interfere, there is a gain of one oscillation every half second, i.e. twice per

second. These two cases are represented in figs. 9 and 10 respectively, which show the two component vibrations and beneath them the variations of the amplitude of the resultant vibration in each case.

2. The Directions of the Component Vibrations are at Right Angles.—In this case the resultant vibration is found by the geometrical addition of the components. The curves obtained by the combination of two mutually perpendicular harmonic vibrations are called **Lissajous*** figures.

Fig. 11 shows the curves obtained by the combination of two mutually perpendicular harmonic vibrations of equal period and equal amplitude but with various phase differences. The component vibrations are drawn as projections of uniform circular motions. If the phase difference is 0 or an even multiple of $\pi/2$, the resultant vibration is **linear**

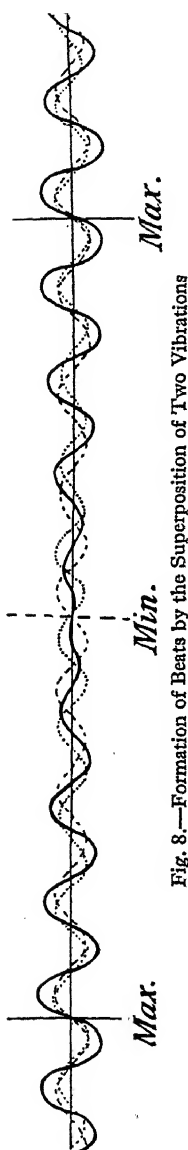
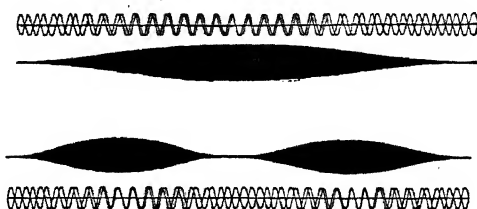


Fig. 8.—Formation of Beats by the Superposition of Two Vibrations



Figs. 9 and 10.—Beats

and harmonic. Every other phase difference gives rise to an elliptical vibration, which becomes circular in the special case when the phase difference is an odd multiple of $\pi/2$. If the frequencies and amplitudes of the two component vibrations are not equal, complicated curves are obtained. A few examples are shown in fig. 12. The phase differences given at the side of the figure refer to the beginning of the vibration; the numerical ratios below refer to the frequencies.

Experimental Tracing of Lissajous Figures.—For this purpose the apparatus shown in fig. 13 (p. 197) may be used.† Four strings each about 3 m. long are suspended from hooks A, B, C and D, screwed into the ceiling at the corners of a square of about 1 m. side. The pair of strings hanging from A and C and the pair hanging from B and D are connected together respectively about halfway down by rings fixed at the ends of a rod EF 1 m. in length. From here the pairs of strings pass down to a funnel-shaped vessel G suspended from them. The funnel has a hole at its point.

When the vessel is displaced slightly in a plane perpendicular to EF it performs harmonic oscillations about EF as axis, the points E and F remaining

* JULES ANTOINE LISSAJOUS (1822–80), French physicist.

† The arrangement is a modification of the “Blackburn pendulum”, devised in 1844, while he was a student at Cambridge, by HUGH BLACKBURN, afterwards Professor of Mathematics at Glasgow.

absolutely at rest. When the vessel is displaced in a plane parallel to EF, the whole suspended system performs harmonic vibrations in this plane. The pendulum length is then the distance from EF to the ceiling, since the triangle EFG cannot swing in this plane. To trace out the vibration figures, fine dry sand is placed in the funnel-shaped vessel and a horizontal board placed beneath it. The sand flowing out traces the figures automatically. By pushing the rod EF up or down, the periods of the two pendulums may be altered in opposite senses and

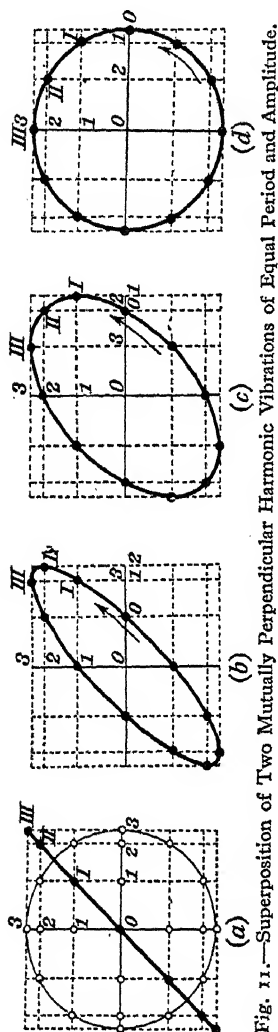


Fig. 11.—Superposition of Two Mutually Perpendicular Harmonic Vibrations of Equal Period and Amplitude.

Phase Differences: (a) 0 ; (b) $\frac{\pi}{6}$; (c) $\frac{\pi}{3}$; (d) $\frac{\pi}{2}$.

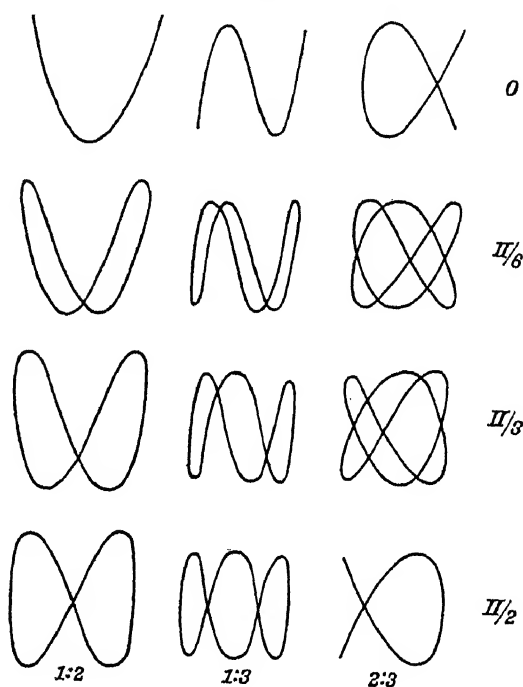


Fig. 12.—Lissajous Figures

hence the ratio of the frequencies varied. In this way it is possible to obtain many other figures in addition to those shown in fig. 12.

The flexural vibrations of the free end of a clamped rod are also harmonic. Attach two pieces of steel of rectangular cross-section (e.g. clock spring) at opposite ends and at 45° to the edges of the opposite longer faces of a block of wood (fig. 14); the two pieces of steel are thus at right angles to one another. They are provided with small mirrors on the inside surfaces of their free ends. A beam of light is made to fall upon one of these mirrors so as to be reflected from it on to the other and then on to a white screen. When one of the springs vibrates, its mirror is rotated according to the sine law and the beam of light produces a bright spot performing harmonic vibrations upon the screen. The same is also true when the second spring vibrates; but in this case the plane of the harmonic vibration is at right angles to that of the first. When both springs vibrate simultaneously, the bright spot also performs both vibrations simultaneously. The

frequencies can be varied by loading the springs with small weights. The curve traced out by the spot of light is a Lissajous figure.

3. Composition of two Oppositely Directed Circular Motions.—The resultant motion of a body performing two congruent, oppositely directed, circular motions simultaneously may be found by the parallelogram of displacements. Such a combination is shown in fig. 15. The orbits are represented by the two

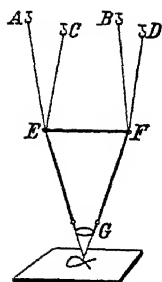


Fig. 13.—Combination of Harmonic Vibrations at Right Angles

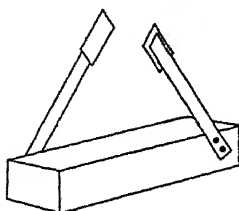


Fig. 14.—Optical Combination of Vibrations

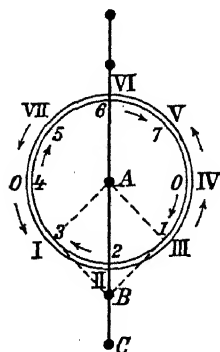


Fig. 15.—Combination of Two Oppositely Directed Circular Motions

circles with centre A, which must be imagined really to coincide. The Roman and Arabic figures mark the successive corresponding positions which the body would have as a result of the respective component motions. The figure shows the graphical combination of the displacements in the positions I and I by the parallelogram construction. The resultant position is at B. The displacement of the extreme point C from the centre is twice the radius of the circle.

The combination of two oppositely directed circular motions of equal radius and period gives a linear vibration with the same period and an amplitude equal to twice the radius of the component circular motions.

Taking account also of the case shown in fig. 11 (d), p. 196, we may sum up by saying:

A circular motion of radius r and period T may be regarded as composed of two linear vibrations of the same amplitude r and period T and with a phase difference of $\pi/2$. A linear vibration of amplitude a and period T may be regarded as composed of two oppositely directed circular motions of radius $a/2$ and the same period T .

3. Forced Vibrations. Resonators

In the cases so far considered we have assumed that the excitation of the vibration consisted of a single impulse, after which the system performed its oscillatory motion undisturbed (**free or natural vibration**). Great importance also attaches to the case in which the excitation is produced by a vibrating system. The phenomena are then very varied and depend upon the ratio of the frequencies and upon the damping in the systems concerned. The following is a mechanical example of such a **forced vibration**, as it is called.

A mass M is suspended by means of a spiral spring F (fig. 16). When displaced from its position of rest by stretching the spring, and then let go, the mass performs the natural vibrations caused by the elastic force of the spring. Now let the point of suspension A be the end of a rod S which itself performs a continuous up and down periodic motion (say by means of a crank drive). We will assume that the mass of the system with which the rod is connected (*the exciter*) is very great in comparison with the mass M suspended from the spring, so that the vibrations of the latter do not react upon the exciter. The system of spring and mass, called the **resonator**, is then forced to perform the vibrations of the exciter. Now how do the amplitude and phase of the resonator depend upon the physical conditions of the two systems?

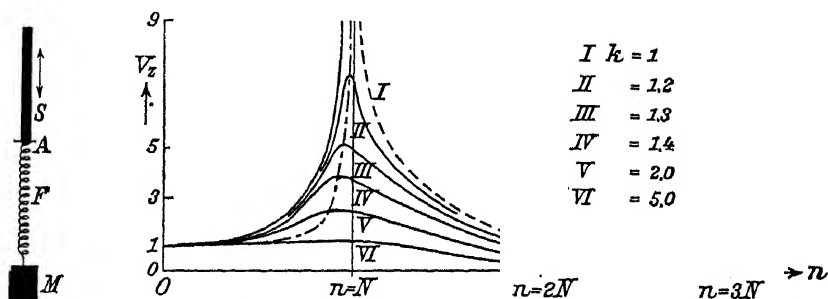


Fig. 16
Forced
Vibration

Fig. 17.—Amplification at Different Frequencies and with Different Damping

1. Amplitude of the Resonator as a Function of the Exciting Frequency n .

Resonator without Damping.—If the frequency n of the forced vibrations is very small compared with the natural frequency N , the resonator exactly follows the motions of the point of suspension. As n increases, the amplitude of the resonator increases more and more until in absence of damping it eventually becomes infinitely great (i.e. the system would be destroyed) when n becomes equal to the natural frequency N . When $n = N$ the natural frequency and the forced frequency are said to be **in resonance**.

If n is further increased, the amplitude of the forced vibration decreases again until, when n is very large, the motion of M consists only of a rapid trembling with very small amplitude. In addition to the forced vibrations the resonator also performs its own natural vibrations. The resultant motion is obtained by superposition as in the examples shown in fig. 6, p. 193.

The uppermost curve of fig. 17 represents the above variations of the amplitude of the forced vibration. The abscissæ are the frequencies of the forced vibration expressed as multiples of the natural frequency N of the resonator.

The ordinates are the corresponding amplitudes of the forced vibration divided by the amplitude of the exciting vibration (*amplification factor*). For $n = N$ the amplification factor is infinite.

Damped Resonator.—When the resonator is damped, the dependence of its amplitudes upon the exciting frequency n is more or less the same as without damping, but even in resonance the amplitude remains finite. With increased damping the maximum amplification also moves towards frequencies smaller than the resonance frequency.

Fig. 17 shows the amplitudes for different damping factors k (p. 192). The dash-dot curve indicates the displacement of the maximum amplification V_x with increasing damping.

Examples.—When an electro-motor of adjustable speed of revolution is placed upon a table, its vibrations, which in general have a frequency about equal to the number of revolutions per second, are transmitted to the table and set this into forced vibration. In the region of a certain quite definite frequency (often of several) very pronounced vibrations are produced; this is when the vibrating systems are in resonance. Large numbers of soldiers are not allowed to march over a bridge in step, because chance resonance might cause damage. Such resonance phenomena are also of great importance in practical engineering. Vibrations of large amplitude may occur in machines with rotating shafts. On account of slight irregularities of running, all engines perform small vibrations with a frequency approximately equal to the number of revolutions per second or a multiple of it. If now at a certain speed of revolution the frequency coincides with the natural frequency of the system shaft + rotating parts, there will be a very great increase of the amplitude of the forced vibrations, which may destroy the machine. Those speeds of revolution of engines at which such resonance phenomena appear are called *critical speeds*.

The cases just considered are also of great importance for the treatment of problems concerning electric oscillations and optical absorption, as well as for the problem of faithful reproduction of sounds by loud-speakers and for the theory of musical instruments.

The apparatus of POHL (fig. 18) is very suitable for the demonstration of forced vibrations*.

The system performing the forced vibrations, or briefly the resonator, consists of a copper wheel to whose axis a spiral spring is attached at 1. Thus it is essentially a balance wheel like that used in watches. Its natural frequency ν_0 is 0.38 sec.⁻¹. Its damping factor can be varied between 1.11 and 2.72 by means of a Foucault current brake W. The periodic force producing the oscillations of the wheel acts at the end 2 of the spiral spring. It is obtained in the simplest manner by means of a connecting rod S fixed eccentrically at E to the axis of a motor (the exciter) whose speed of revolution can be varied at will.

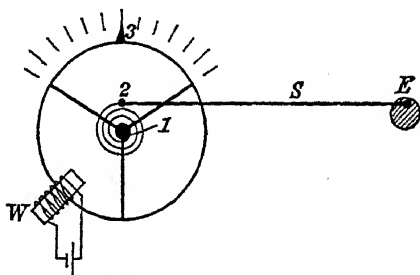


Fig. 18.—Principle of Pohl's Vibration Apparatus

* R. W. Pohl, *Physical Principles of Mechanics and Acoustics*, p. 254.

2. Phase of the Resonator for Different Exciting Frequencies.

Resonator without Damping.—In this case the phase of the resonator coincides exactly with that of the exciter for all frequencies n smaller than the resonance frequency N . For all frequencies greater than N , however, the phase is altered by π , i.e. the resonator vibrates in the opposite direction to the exciter. Thus the phase suddenly changes by π in passing through the resonance frequency.

Damped Resonator.—Here the phase difference gradually increases. For very slow forced vibrations it is very small, increases with increasing frequency in a manner dependent upon the degree of damping,

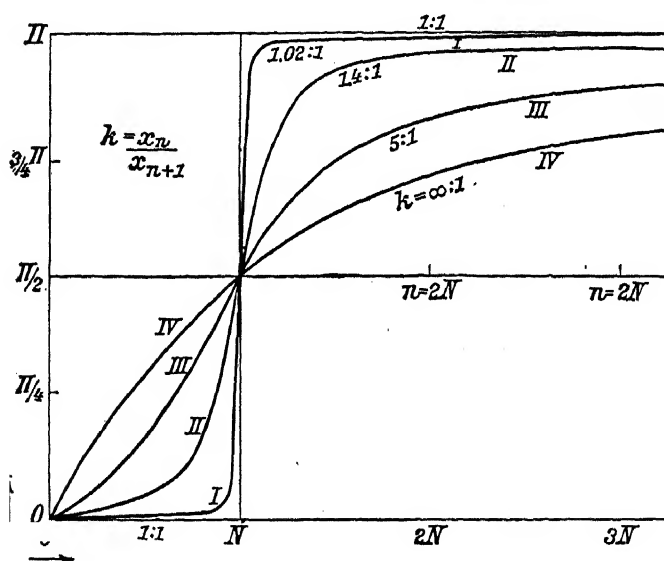


Fig. 19. —Phase Difference as a Function of the Frequency with Different Damping Factors (N = Resonance Frequency). Ordinates, phase difference. Abscissæ, frequency

and finally always reaches the value $\pi/2$ at resonance. The resonator is then in its position of greatest displacement when the exciter is just passing through its equilibrium position. Fig. 19 shows the phase differences as a function of the exciting frequency for different damping factors. In absence of damping ($k = 1$) the curve runs from 0 to N along the axis of abscissæ, and for $n > N$ parallel to this axis at a distance π from it.

The phase differences can be demonstrated very well with the above-mentioned apparatus of POHL. They play an important part in applied electricity, and in cases where complicated vibrations have to be registered true to phase. They have found practical application in Frahm's anti-rolling tank (p. 202).

4. Coupled Vibrations

In the previous paragraph it was assumed that the resonator did not react upon the exciter as in the mechanical example quoted. We will now consider systems which are equivalent to one another in that the resonator can react without restriction upon the exciter. Such systems are said to be **coupled**.

1. There is in general a continual interchange of energy between the coupled systems.

Experiment.—Hang two heavy bodies (e.g. kilogram weights) as pendulums from the ceiling at a distance of 50 cm. apart on the ends of two threads 2 m. long (fig. 20). Since their lengths are equal, these pendulums have equal periods. Connect the two suspending threads about half-way up with a cross thread about 70 cm. in length, and load it in the middle with about 50 gm. wt. Now set the first pendulum swinging in a plane perpendicular to that passing through the common equilibrium position of the whole system. In swinging, the first pendulum lifts the weight hung upon the connecting thread, which thus exerts a pull upon the second pendulum. A certain time is necessary for the transmission of this pull from the first pendulum to the second. As a result, the second pendulum is also set swinging and the first loses a part of its kinetic energy. Since the first pendulum is always in advance of the second, it accelerates the latter and is itself retarded somewhat every swing; its amplitude is thus gradually diminished. After about 10 swings the first pendulum has given up the whole of its energy to the second, and has therefore come to rest, while the second pendulum is swinging with the full amplitude, i.e. with the amplitude which the first pendulum originally had.

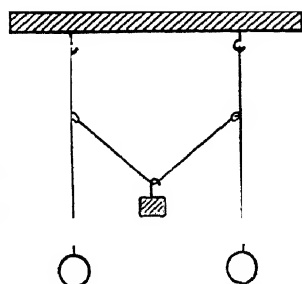


Fig. 20.—Coupled Vibrations
(after Oberbeck)

From this point onward the second pendulum assumes the rôle of the first and begins to transmit during every swing a part of its energy back again to the first, until this eventually swings once more with its full original amplitude and the second pendulum is once more at rest.

If the weight which acts as coupling is replaced by another twice as great, the coupling becomes "tighter" than before, since the force between the two pendulums is greater. The complete transmission now takes only five swings instead of ten. If the coupling is still tighter, i.e. if the connecting thread is still more tightly stretched, the transmission takes place in still shorter time.

The coupling can also be loosened or tightened by raising or lowering the connecting thread.

2. If the natural frequencies of two systems before coupling are N_1 and N_2 respectively ($N_1 < N_2$), every part of the coupled system vibrates with two frequencies n_1 and n_2 such that $n_1 < N_1$ and $n_2 > N_2$. The superposition of these two frequencies gives rise to beats (p. 194) which become apparent in the energy exchanges between the two systems. The above experiments show that the looser the coupling, the less the difference between the two coupled frequencies;

for the energy exchange then takes place more slowly, i.e. the beat frequency is smaller. Thus the looser the coupling the longer the beat period. Even when the two systems have the same natural frequency $N_1 = N_2$, two frequencies are produced by coupling and hence beats appear.

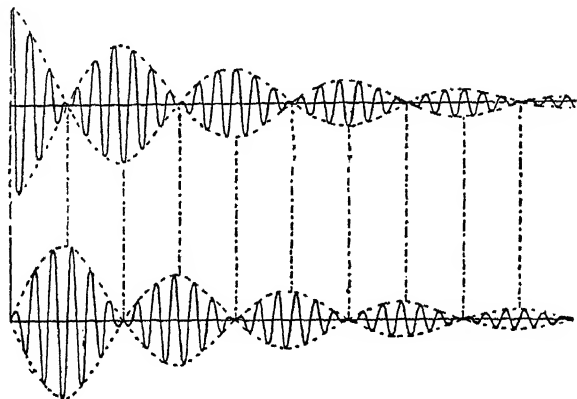


Fig. 21.—Coupled Vibrations of Damped Systems
Primary System, above; Secondary System, below

3. When both vibrations are damped, the resultant beats are also damped. Fig. 21 gives an example of the behaviour of two such coupled systems. This case is of great importance, especially in connexion with electrical oscillations (see Vol. III for the treatment of the example of fig. 21).

The Frahm anti-rolling tank is an example of the practical application of coupled vibrations.

When the frequency of the waves striking a ship is approximately in resonance with its natural frequency, the ship may be displaced very considerably from its mean position, since each successive wave increases the effect of the previous one. The ship then "rolls" badly.

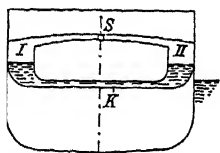


Fig. 22.—Frahm Anti-rolling Tank

There is, however, a phase difference of $\pi/2$ (p. 200) between the motion of the ship and that of the waves (resonance case $n = N$), so that the latter strike the ship most vigorously just as it is passing through its position of rest. To damp this "rolling" a tank may be employed (i.e. a system coupled to the ship). This is built into the ship in the manner shown in fig. 22 and is about half filled with water. It is made in two parts, I and II, communicating with one another by means of a channel K. It is essential that the dimensions be so chosen that the natural frequency of the water in the tank is equal to that of the ship (p. 189).

The rolling of the ship sets the water in the tank swinging, and this reacts back upon the ship owing to the inertia and displacement of the weight of the tank water. Since the oscillation is in resonance with that of the ship, there is a phase lag of $\pi/2$. There is therefore a difference of π between the phase of the waves striking the ship and that of the oscillating tank water. Hence the tank water oscillates in exactly the opposite direction from the waves and thus protects the ship against too great rolling.

The valve S serves to regulate the flow of air between the two parts I and II of the tank, and permits of the regulation of the damping of the tank water oscillations to suit the strength of the waves. The effect of the anti-rolling tank can be seen from fig. 23, which shows the rolling motion of a ship with and without the device.

Note.—The impact of two elastic masses can also be regarded as a case of coupled vibration in which the vibrations are caused by the elastic deformations. Here the coupling is so tight that even after a quarter of a period the energy transmission to the second body is complete. When, for example, an ivory ball hanging

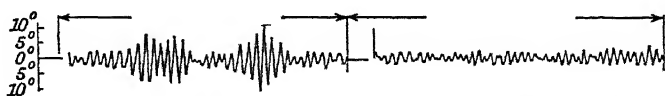


Fig. 23.—Effect of the Anti-rolling Tank (each half of the figure represents a period of 8 minutes)
(Left: without tank. Right: with tank)

from a thread strikes against another similar ball also hanging from a thread of the same length, the total energy of the first ball is transferred to the second by the impact. On account of the freedom of motion the coupling is at once removed and hence the second ball retains the whole of the energy.

5. Propagation of Energy through a Series of Coupled Systems

1. We will now consider a series of similar pendulums hanging side by side and coupled together as in the simple case shown in fig. 20 (p. 201). When the first pendulum is set swinging, the second gradually takes over the motion as explained, while the first gradually loses its energy. In the case at present under consideration, however, the subsequent pendulums will also be set swinging and the first one will rapidly come to rest. Thus the energy is propagated from the one end right through the series.

This propagation can be demonstrated in a very elegant manner by means of the following apparatus (after JULIUS) in which the pendulum swings are replaced by torsional oscillations. At the upper and lower ends of a stand 2 m. in height are fixed horizontal cross bars bearing small hooks (figs. 24 and 25). To these are attached two thin threads about 25 cm. long, which are joined respectively to the upper and lower ends of a steel wire, which passes freely through two clamps; but they permit it to turn about its own axis without producing a turning moment sufficiently great to influence the present experiments.

Horizontal brass rods can be attached to the steel wire by means of suitable clips. The moment of inertia of these rods is increased by loading them at the ends with small bulbs. We will first attach *only one* such rod. Then by the application of an instantaneous displacing moment it can be set into rotation about the steel wire as axis. The wire turns also without resistance, since the two threads by which it is stretched do not exert any appreciable torsional forces. The rotational motion of the whole therefore takes place with approximately uniform angular velocity. But if the steel wire be clamped tightly at one or both ends, the single brass rod will perform harmonic torsional vibrations about it.

Now let us attach *two* cross rods as shown in fig. 24. For the present we will leave both ends of the wire free, i.e. not clamped, and will set the lower rod into

rotation by an instantaneous displacing moment. This twists the part of the steel wire between the two rods, thus producing a moment which acts upon the respective rods with equal magnitude and in opposite senses. The result is that the lower rod is retarded and the upper one accelerated. After a while the lower

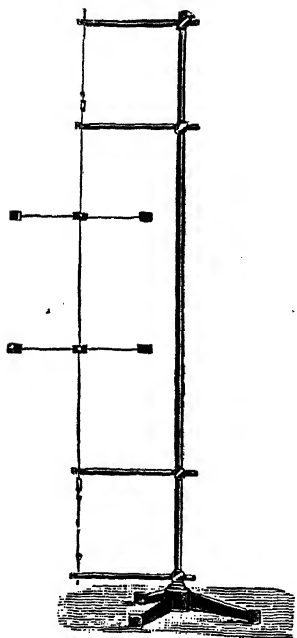


Fig. 24.—Coupled Torsional Vibrations

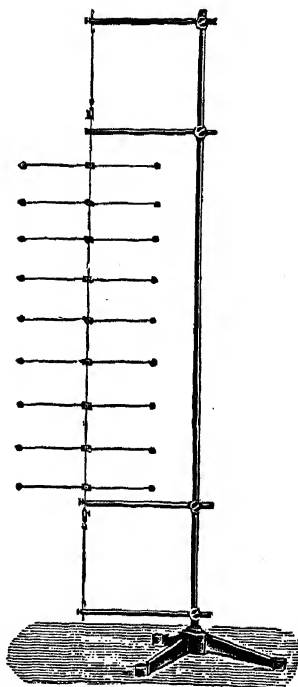


Fig. 25.—Wave Apparatus (after Julius)

rod comes completely to rest, by which time the upper one has assumed a motion exactly identical with the original motion of the lower one.

The rotation of the upper rod now twists the portion of the wire between the rods in the same manner as before, and the interchange of energy is reversed. Thus the whole energy passes alternately from the one rod to the other. The course of this process is determined only by the moment of inertia of the masses and the torsion they produce in the steel wire.

We now attach a larger number of similar cross rods to the steel wire as in fig. 25. The ends of the wire are allowed to remain free as before. When the lowest rod is made to rotate, the initial stages of the process are just the same as described above. But even while it is being turned by the torsion of the lowest section of the wire, the second rod is giving up a part of its energy to the third owing to the twisting of the portion of the wire between them. Thus the third and successive rods are gradually set rotating, while the rotation of the lowest one is retarded. After a while the lowest rod comes completely to rest after turning through a certain angle depending upon the magnitude of the original moment applied. Each subsequent rod then performs exactly the same rotation through exactly the same angle and then also comes to rest. Thus the rotation is transmitted right up to the topmost rod.

2. Behaviour of the System at the End of the Series. Reflections.—When the energy reaches the end of the series it turns back and passes

along the series in the opposite direction: it is then said to have been **reflected**. The reflection takes place without loss of energy, but the relation between the phases of the incident and reflected vibrations depends upon whether the end of the series is fixed or is itself free to vibrate.

When the end is free, there is no phase change on reflection; when the end is fixed, the phase is reversed.

This behaviour can also be demonstrated by means of the apparatus already described. In the last experiment the topmost cross rod is subjected to no elastic resistance, since the upper end of the steel wire can rotate freely. Hence this rod goes on rotating until it has completed twice the angle turned through by the other rods. It thus reacts back upon the lower rods by virtue of the elastic torsion of the sections of the steel wire, and the rotation is transmitted downwards again in the same manner as it was transmitted upwards. The sense of the rotations of the individual rods remains the same as that of the original displacement. The process is repeated a number of times, until finally the general resistances to motion interfere with its normal course and bring it to an end.

We will now clamp the upper end of the steel wire and once more set the lowest rod into rotation. The first stages of the process are exactly the same as described above; but when the disturbance has reached the upper end, the topmost rod cannot perform its rotation without resistance, since it must twist the topmost section of the steel wire. The result of this torsion is a reaction upon the topmost rod itself, in consequence of which it not only comes to rest very soon, but swings back again into its initial position under the influence of the elastic stress of the topmost section of the wire. It now reacts back upon the rods beneath it, causing them all to rotate successively in the opposite direction from that of their initial rotation. If in the meanwhile the lower end of the wire has also been clamped, the motion passes down to the lowest rod, which is again unable to rotate freely. It therefore produces an elastic twisting of the lowest section of the wire and this causes the lowest rod to swing back. This backward rotation is then transmitted back up the series again in the manner already described.

3. Transmission of Energy along a Series of Elastic Systems when Struck.—Several equal elastic spheres are hung up touching one another (fig. 26). When the first sphere A impinges on the second, the energy is transmitted completely from the first to the second. The second transmits it to the third, the third to the fourth, and so on. The last sphere C moves off with the same energy as that possessed by the first before impact, and therefore rises to the same height as that from which A originally fell.

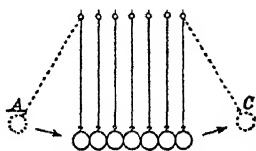


Fig. 26.—Transmission of Energy by Impact

The transmission of energy takes place in accordance with the laws and formulæ regarding elastic impact derived in § 5, p. 214, Vol. I. Now it must be remembered also that a certain time is required for the transmission of the energy from the first sphere to the last. If we

assume that the row of spheres is so long that this transmission takes one second, we can call this length, which is the distance covered by the energy in one second, the *velocity of propagation*. It is greater than the velocity of impact of the first sphere. Thus the last sphere moves off sooner than the first would have arrived at the far end of the row if it had been moving freely.

The process of transmission can be regarded as equivalent to the motion of a body with uniform velocity; the whole of the mass of the body does not move at once, however, but the *state of motion* is transmitted from sphere to sphere along the whole row, each individual sphere only moving through a very small distance.

In connexion with this case it is very instructive to notice that when the first sphere impinges upon the row its energy is not transmitted to all the other spheres so that they each take up a fraction simultaneously. Actually they all remain at rest and the last one receives the whole of the energy of the first. This is due to the fact that the transference is not instantaneous, but requires a certain time ($\frac{1}{2}$ period), so that the remaining spheres do not act as one mass. It is also clear from this that the velocity of propagation of the energy depends upon the period of the elastic vibrations, i.e. essentially upon the elastic properties of the system.

The case just considered is very important; for if we imagine the spheres to be connected rigidly together, we obtain an elastic rod. The above considerations therefore hold quite generally for the propagation of a disturbance in an elastic medium. The velocity of such a propagation has already been calculated in § 6, p. 217, Vol. I.

4. Reflection at the Junction of Rods of Different Mass per Unit Length.—Consider an elastic rod with another rod of the same material but of smaller cross-section joined on to it at one end. The energy of a blow upon the other end of the first rod is propagated along it until it reaches the junction; then a fraction of it passes over into the thinner rod exactly as in the impact of one elastic sphere against another of smaller mass. The thinner the second rod, the smaller the fraction of the energy that passes into it. The remainder is reflected without alteration of phase.

If the second rod is of the same material as the first but of greater cross-section, the energy is again partially reflected from the junction, this time with reversal of phase. A part of the energy passes into the wider rod exactly as in the impact of one elastic sphere against another of greater mass.

These phenomena can also be observed well with the apparatus shown in figs. 24 and 25 (p. 204), if the moments of inertia of a group of the cross bars are increased by attaching larger weights to their ends.

A disturbance passing along one part of a rod is reflected without change of phase at the junction with a second part when the mass per unit length of the second part is less than that of the first. The reflection is accompanied by a reversal of phase when the mass per unit length of the second part is greater than that of the first.

In both cases there is a partial loss of energy from the first part to the second.

5. Longitudinal and Transverse Transmission.—In the experiments with a row of spheres or an elastic rod described above, the direction of motion of the individual parts was the same as (or opposite to) the direction of propagation of the energy. This is known as **longitudinal transmission**. In the experiment with the two pendulums (fig. 20, p. 201) the direction of swing was at right angles to the direction in which the energy was transmitted between them. This is known as **transverse transmission**.

Further Examples.—1. The propagation of a transverse impulse can easily be observed by stretching a long rubber tube (about 10 m.) horizontally and then striking it a short sharp downward blow at one end. It will be seen that the downward motion of the individual parts is propagated along the tube and then reflected at the opposite end in such a way that the downward motion is converted into an upward motion. This is the phase reversal which always accompanies reflection at a fixed end. The phenomenon can be especially well followed if the tube is filled with water, since this increases its mass and diminishes the speed of propagation of the disturbance.

If the far end of the stretched tube be attached to one end of a long thread (i.e. a body of smaller mass per unit length) the other end of which is tied to a fixed wall, the reflection at the junction now takes place without change of phase. Since, however, the thread has a certain mass, a fraction of the energy passes over into it and the reflection is therefore accompanied by diminution of amplitude.

2. An open narrow vessel at least 2 m. in length and with parallel sides is partially filled with water. A body is dipped into the water or a stone or drop of water is allowed to fall into it at one end of the vessel. The individual water particles are thereby set into a circular motion, as can be seen from the movements of light suspended bodies such as fragments of sawdust. Each particle moves only once around its circular path, thereby transmitting its energy to the next and coming to rest itself. In this way the initial disturbance is transmitted right along to the end of the vessel. An elevation or crest and two depressions or troughs are observed to move over the surface of the water and to be reflected at the far end. The force effecting the transmission is in this case the force of gravity upon the water particles, by virtue of which there is a tendency for differences of level between neighbouring portions of the surface to be equalized. Thus gravity plays here the part of the coupling. The transmission of such disturbances upon the surface of water is not purely transverse, since the circular motion of the individual particles also has longitudinal components.

CHAPTER II

Wave Motion

1. Introductory Observations upon Water Waves

1. Formation of Wave Trains.—In the experiments so far described there was only a single impulse, so that each individual particle only performed its motion *once*. The first particle may, however, be made to vibrate continuously. For example, the first cross rod of the wave apparatus (fig. 25, p. 204) may be displaced at once in the opposite direction every time it comes to rest, or in the last example a series of drops allowed to fall into the water at such a rate that each gives rise to a new disturbance as soon as the preceding disturbance has been passed on. In these cases each successive impulse is transmitted in the same way as the first, so that the whole series of cross rods or the whole surface of the water performs vibrations, each particle going through the same motions as the preceding one but a little later. If we assume that the wave apparatus or vessel of water is infinitely long, we need take no account of the backward motion produced by reflection at the end. We then have a **wave system** or **wave train**.

The production of water waves* is represented in fig. 1. In the top figure the water surface is at rest. When it is disturbed, the points numbered 0 to 15 move in circles with constant velocity. When the particle 0 has completed $\frac{1}{2}$ of its circle, the particle 1 begins to move. By the time the particle 0 has completed $\frac{3}{2}$ of its circle, the particle 1 has completed $\frac{1}{2}$ of its circle and the particle 2 begins to move. This state is represented in fig. 1 II. Similarly figs. IV to XII show the states of motion after completion by each particle of a further $\frac{2}{2}$, $\frac{4}{2}$, &c., of its circular orbit. Thus, for example, in fig. VI the zero particle has completed $\frac{5}{2}$, the first particle $\frac{3}{2}$, the second $\frac{1}{2}$, the third $\frac{5}{2}$, the fourth $\frac{3}{2}$, and the fifth $\frac{1}{2}$ of its circular motion, while the sixth particle is just about to begin to move. At this moment the zero particle has arrived once again at the original water level; it is not in its original state of motion, however, but is now moving upwards instead of downwards. Only after it has completed the whole of its circular orbit does the zero particle arrive at its initial position and its original state of motion. At this moment, which is represented in fig. XII, a complete wave has been formed. The twelfth particle is then in the same state of motion as the zero particle, while each intermediate particle is in advance of the one preceding it by $\frac{1}{2}$ of its complete cycle.

* Experimental investigations of wave motion were carried out in 1825 by the brothers F. H. WEBER and WILHELM WEBER of Leipzig.

Fig. 1 XII shows how a part of the water has risen above the original level and a part has sunk below it. The former is called a **crest**, the latter a **trough**. The distance of the zero particle from the twelfth is called the **wave-length**. The difference in height between the normal level and the top of the crest or bottom of the trough is

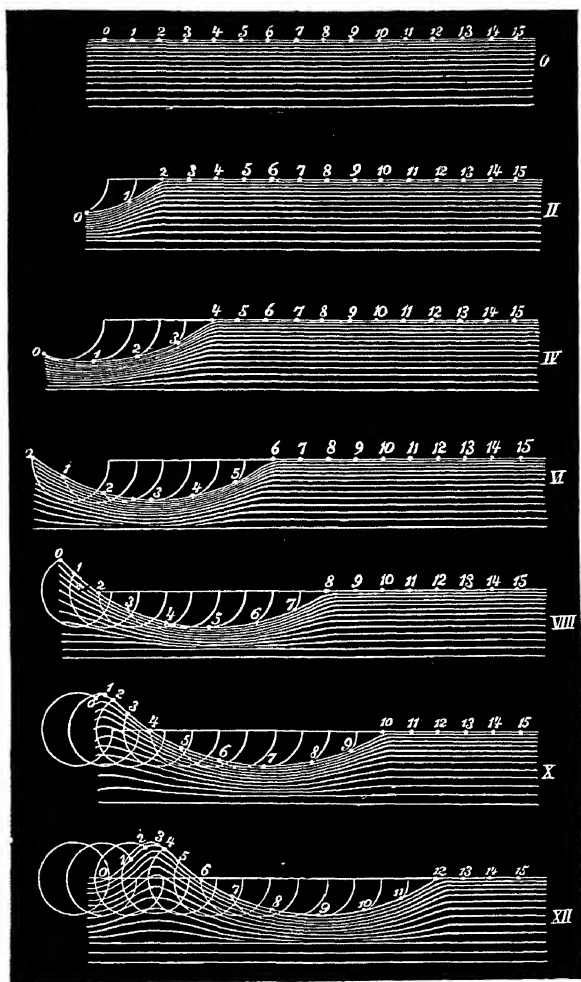


Fig. 1.—Formation of Water Waves by the Circular Motion of the Individual Particles (after the brothers Weber)

the **amplitude** of the wave. *In the case of a water wave the crest and trough are not of the same shape; the crest is shorter and steeper than the trough.*

The wave motion can only be kept up in this form, provided that the zero particle is given a continuous series of suitably timed impulses.

When the free water surface is of *large area* and the zero particle

is situated somewhere in the middle of it, the waves extend in all directions. Thus the farther the wave spreads out from the centre of disturbance, the larger the mass of water to which the kinetic energy is transmitted. If the amount of kinetic energy initially imparted to the zero particle is $\frac{1}{2}Mv^2$, then when the mass of water set in motion has become four times as great, the kinetic energy must be expressible

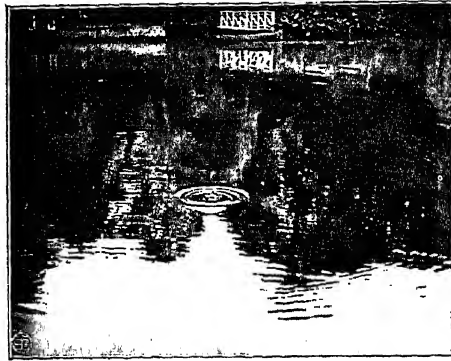


Fig. 2.—Circular Wave Train

in the form $\frac{1}{2} \cdot 4M \cdot (\frac{1}{2}v)^2$. The velocity with which the fourfold mass of water passes through its position of equilibrium is thus only half as great as the original velocity imparted to the zero particle. In other words, the amplitude of the wave decreases with increasing distance from the centre of disturbance; for, other things being equal, the smaller the velocity of passage through the equilibrium position, the smaller also the amplitude.

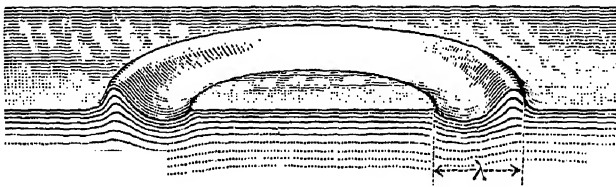


Fig. 3.—Single Circular Wave (diagrammatic)

In the experiment with the water wave in the narrow vessel with parallel walls there was no such decrease of amplitude (neglecting the effect of the friction of the particles against one another and against the walls), because the mass of water subsequently set in motion is never greater than that originally disturbed.

2. Observations on Single Waves.—When a stone is thrown into water or a drop allowed to fall on to the surface, a circular wave train consisting of a small number of crests and troughs spreads out from the disturbed point, while after a time no more motion can be seen at the centre itself. Fig. 2 is a reproduction of a photograph of a wave produced by throwing a ball into water. Fig. 3 shows a diagrammatic section through a single circular wave of wave-length λ .

In actual experiment the circular wave is preceded by a large number of

smaller waves of quite different appearance, particularly of much smaller amplitude. The reason for this twofold wave is that the stable equilibrium state of the water surface is determined by two different forces, gravity and surface tension. The main wave is due to gravity and the smaller ones to surface tension. The latter are called **capillary waves**. Each of the two types must be considered separately. Here we will only consider the **gravitational waves**.

It is clear that when the initial disturbance is only of short duration, only a few waves will spread out from the centre; for the whole energy of the disturbance is passed on completely to the neighbouring water masses in a short time.

The velocity with which a water wave spreads out, i.e. the velocity with which a particular part of the wave advances radially from the centre, is independent of the amplitude. When the depth of the water is small in comparison with the wave-length, the velocity is also independent of the wave-length (but dependent upon the depth of the water). When the depth is greater, the velocity increases as the depth increases and then also with the wave-length, until for very great depths it reaches a limiting value only dependent upon the wave-

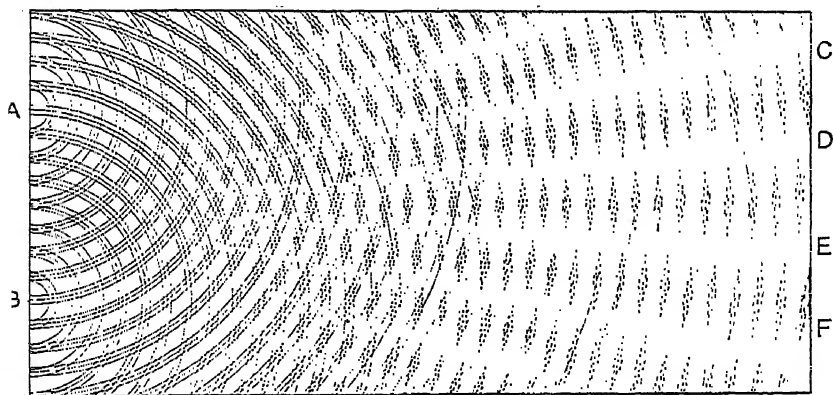


Fig. 4.—Interference or Superposition drawn for two sets of ripples originating at A and B

length. In the case of shallow water, e.g. near a coast, an observant person can draw conclusions as to the depth from the behaviour of the waves. Those parts of an incoming wave which pass over shallows lag behind those which pass over places where the water is deeper. Sea waves caused by strong winds may have a wave-length from 50 to 150 m., an amplitude of about 10 m. and a velocity of advance of from 10 to 15 m. per sec.

3. Interference of Single Waves.—When two similar stones or drops are allowed to fall simultaneously into water at some distance apart, the two congruent wave systems produced spread out with equal velocities from their respective centres. After a time they penetrate each other, and we observe the effect shown in fig. 4.

It is seen (cf. also fig. 7, p. 214) that at points corresponding to crests in both systems there are crests of double height, and at points corresponding to troughs in both systems there are troughs of double depth, but at points corresponding to a crest in one system and a trough in the other there is no difference in level as compared with the free surface at rest. As the waves spread out these points preserve their mutual positions with only slight displacements. The crests of

double height and the troughs of double depth move along the perpendicular bisector of the line joining the two centres. Thus along this perpendicular moves a short wave of double amplitude, while on both sides of it the water surface remains approximately at rest. If the movement of the middle of this wave be noted at different points separated by equal time intervals, its velocity is found to be very great at first and then to decrease gradually until it finally becomes equal to the velocity of the primary waves. The points of minimum amplitude on either side move with approximately constant velocity away from the line joining the two centres and gradually diverge from the perpendicular bisector.

The points of maximum elevation and depression lie on the perpendicular bisector of the join of the centres of disturbance, because this is the locus of points equidistant from these centres and hence of equal phase in both wave systems. For the points of minimum amplitude, on the other hand, the difference of the distances from the centres must be half a wave-length. The locus of such points is a hyperbola whose transverse axis is equal to half the wave-length of the primary waves. The points move along the branches of this hyperbola with a velocity which is at first great and then decreases.

If three stones or three drops are let fall into water simultaneously in such a way that the three centres of disturbance lie upon a straight line at equal distances, three circular waves I, II and III are produced. As a result of the interference* of I with II and II with III, points of maximum and minimum amplitude are produced as already described. In addition, points of double amplitude also appear where the waves I and III cross with like phase, i.e. upon the perpendicular bisector of the line joining the respective centre. These points also move at right angles to the line of centres and are accompanied on either side by points of approximately zero amplitude.

The result of further increasing the number of disturbances upon a straight line is to produce further repetitions of the above effect. A system of points of maximum amplitude appears and moves at right angles to the line joining the centres of disturbance. The points of minimum amplitude, which move laterally when at relatively great distances from the centres, are of no effect. When a large number of points lying side by side upon a straight line are disturbed simultaneously by throwing a rod horizontally on to the surface of the water, circular waves spread out from the ends of the rod, while straight waves parallel to the rod move out perpendicular to it.

In the case of a rod in the form of an arc of a circle, each element can be regarded as straight. Neglecting the circular waves spreading out from the ends, a circular wave of great amplitude must therefore be sent out from each side of the rod. The centre of curvature of these waves will coincide with the centre of the circles of which the curved rod forms an arc. In this case it is possible to observe how the amplitude of the wave sent out from the concave side of the rod increases as its energy is concentrated into ever decreasing masses of water. Conversely, the amplitude of the wave from the other side of the rod becomes smaller and smaller. The total wave produced by the superposition of a large number of small individual waves is called a **wave front** to distinguish it from the **elementary waves** spreading out in circles from the individual points of disturbance.

4. Observations upon Wave Systems.—In order to produce a system or train of circular water waves the water must be made to vibrate up and down by continued periodic impulses, so that energy

* The principle of interference was used by NEWTON to explain certain tidal phenomena, but was first definitely stated about 1800 by THOMAS YOUNG in his celebrated papers on the Wave Theory of Light.

is continuously supplied to the wave system. Thus, for example, the **central wave system** shown in fig. 5 was produced by moving a ball up and down continuously at the centre.

Being reproduced (like the other pictures of water waves) from a photograph, the shape of the waves in fig. 5 is modified by the perspective. The waves are represented as they actually appear to the eye. The ellipses of the figure correspond therefore to concentric circles seen in perspective.

We now excite two neighbouring points simultaneously by means of a fork-shaped wire attached to a vibrating rod. Two exactly similar circular wave systems spread out from the two points where the ends of the wire dip into the water. The interference of the crests and troughs of the two systems gives rise to hyperbolas as already discussed above (see also fig. 4, p. 211).

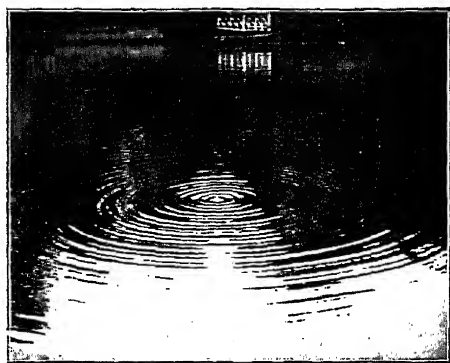


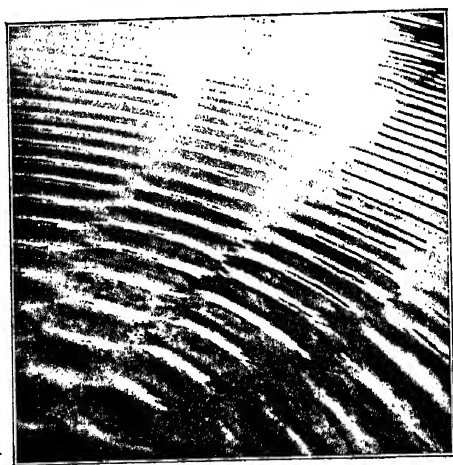
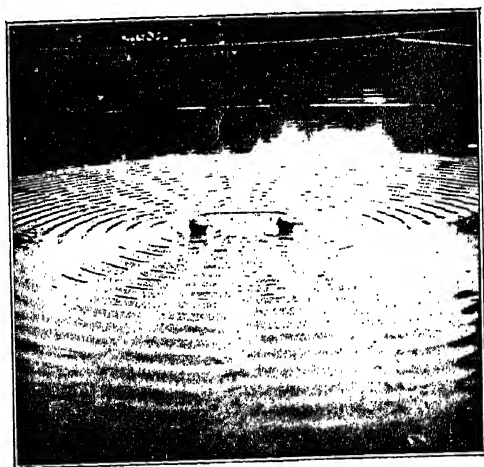
Fig. 5.—Central Wave System

Fig. 6 shows a photograph of the effect produced by the interference of two central wave systems. These were produced by two wooden balls suspended a short distance apart from a rope stretched across a smooth lake. The rope was set vibrating and the wooden balls thus made to dip periodically into the water. The first interference hyperbolas on each side of the perpendicular bisector of the line joining the balls correspond to a phase difference of half a wave-length between the interfering wave trains. The successive hyperbolas on each side correspond to phase differences of $\frac{3}{2}$, $\frac{5}{2}$, . . . wave-lengths. The wave centres are the common foci of all these confocal* hyperbolas. At great distances from the centres of disturbance the hyperbolas may be regarded as identical with their asymptotes; the interference lines are then straight. In fig. 7 a part of the interfering systems is reproduced on a larger scale. Particular attention is called to the fact that the waves on opposite sides of the interference hyperbolas have opposite phase, i.e. that a crest on one side of a hyperbola comes opposite a trough on the other side.

In fig. 8 six points at equal, short distances along a straight line were excited simultaneously. In the immediate neighbourhood of these

* Lat., *con*, together; *confocal*, with common focus.

centres there is a relatively complicated system of crests and troughs. Rather farther out on the right of the figure, however, straight wave fronts are seen to be formed. The direction of their propagation is at right angles to the line through the centres of disturbance, i.e. in the figure from left to right. If a still larger number of points be excited



Figs. 6 and 7.—Interference of Two Wave Trains

simultaneously, the confusion in their immediate neighbourhood vanishes completely and a straight wave front is formed at once.

Such a straight wave front can be produced by attaching a long narrow strip of metal to the end of a vibrating rod so that it dips periodically in the water. Alternatively the edge of a board may be moved periodically backwards and forwards in the surface. The right-hand side of fig. 9 (p. 215) shows such a straight wave front, the direction of whose motion is from right to left.

5. **Huygens' Principle.***—Parallel to the oncoming straight wave front we place in the water a screen consisting of a vertical board with a narrow slit-shaped aperture in it. We then observe a completely new phenomenon (fig. 9). The wave does not move on in a straight line beyond the aperture, but the motion of the water in it gives rise to a new wave centre from which the wave spreads in circles behind the screen.

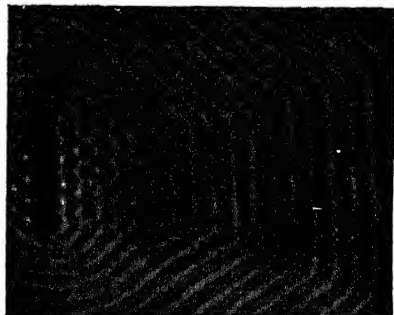


Fig. 8.—Interference of Six Wave Systems with Centres upon a Straight Line

From this experiment it follows that we are justified in regarding every individual point of a wave system as a new wave centre. If we make three openings in the screen, each of these acts as a new centre. When the number of openings is still further increased, the result becomes identical with the right-hand side of fig. 8 above, i.e. a new straight wave front is formed behind the screen. If now we imagine



Fig. 9.—Circular Wave emanating from the Aperture in a Screen

an even greater number of such openings side by side, so that the portions of the screen between them become negligible, we eventually

* CHRISTIAN HUYGENS (also spelt HUYGHENS), born 1629, died 1695 at the Hague, the most important scientist of his time, and a prominent member of the newly founded Academy of Sciences in Paris. He may be regarded as one of the founders of modern physics. He made pioneer investigations of the compound pendulum, in which he originated the concept of moment of inertia. He invented the pendulum clock and the type with balance wheel regulation, and occupied himself with many other physical, astronomical and mathematical problems. He was the founder (1678) of the wave theory of light (*Traité de la Lumière*, 1690), although this had previously been suggested, as he himself admits, by the Jesuit father IGNATIUS PARDIES (1638–73) and by R. HOOKE.

arrive at the case in which the screen is not there at all. In spite of this, each of the points where the screen was can be regarded as the centre of a new elementary circular wave. This consideration embodies the ideas underlying Huygens' principle:

*Every point of a wave can be regarded as the centre of a new elementary wave. The resultant wave produced by the interference of all these elementary waves is identical with the original wave.**

6. Reflection of Waves.—The phenomenon of reflection of waves can be understood in the light of Huygens' principle. On the right-hand side of fig. 10 can be seen a portion of the board by whose periodic

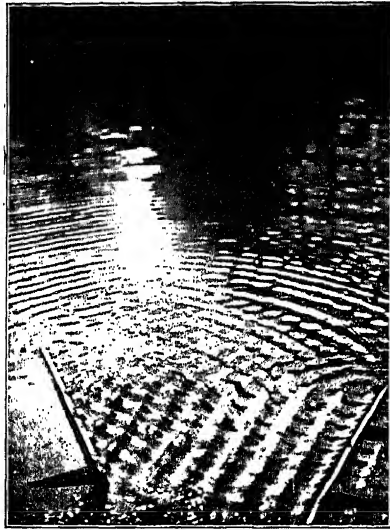


Fig. 10.—Reflection of Plane Waves

motion a straight wave front is produced. The circular wave system sent out from the end of the board can also be seen; this is of no importance for the present considerations. The straight wave front moves from right to left and is incident against a fixed board. The portions of the board lying farthest to the right in the figure are first struck by the wave front. Each point of incidence upon the reflector can be regarded as a new centre of excitation from which elementary circular waves are sent out. The portions of the fixed board lying farther to the left are struck later and thus in turn become new centres of elementary waves. By the interference of all these elements a new system of straight wave fronts is formed. These move off diagonally upwards to the right, in contrast to the incident waves which ap-

* It may be remarked that HUYGENS' principle, while of great service in many cases, does not hold with strict mathematical accuracy. A rigid formulation of it was given in 1882 by KIRCHHOFF; but this can hardly be explained without extensive use of mathematical symbols. For further information the reader is therefore referred to textbooks of mathematical physics.

proached the board diagonally upwards to the left. The incident straight wave system is therefore reflected. The angle of incidence (i.e. the

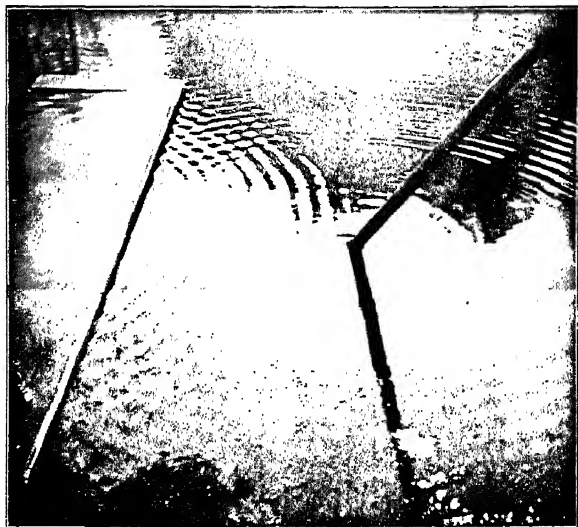


Fig. 11.—Reflection of Circular Waves at a Straight Wall

angle between the direction of incidence and the normal to the reflecting surface) is equal to the angle of reflection (i.e. the angle between the direction of the motion of the reflected wave and the normal).



Fig. 12.—Reflection of Straight Waves at a Concave Wall

The reflection of a circular wave system at a fixed wall (see fig. 11) takes place in the same way. The centre of the reflected circular waves lies as far behind the wall as the centre of the incident circular waves lies in front of it.

Fig. 12 shows the reflection of a straight wave front at the concave side of a

wall having the shape of a circular arc. Since the incident wave front strikes the outer ends of the reflector first, new elementary waves are formed here sooner than in the middle. In this way a new circular wave system is set up. Its direc-

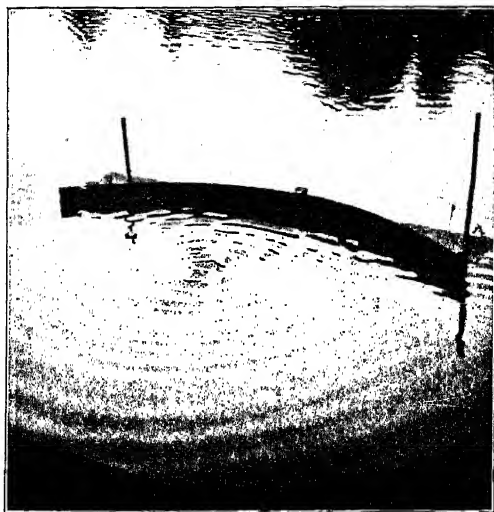


Fig. 13.—Reflection of Waves emanating from a Focus

tion of motion is towards a point, which appears as a dark spot in the figure. Thus the reflected waves converge towards this point (the *focus*).

Conversely, if we excite a circular wave system with its centre at the focus of the concave wall (fig. 13), the waves so produced strike the middle parts of the wall before the outer parts. New centres of elementary waves are thus formed

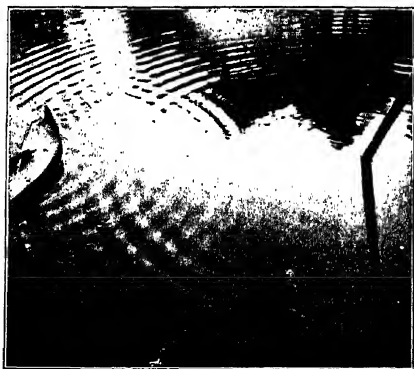


Fig. 14.—Reflection of Circular Waves at a Convex Wall

first at the centre and later at the outer points of the reflector. The interference of all these elementary waves produces a straight wave front: the incident circular wave system is reflected as a system of straight wave fronts.

Fig. 14 shows the reflection of a circular wave system from a convex circular wall. The reflected system is also circular, but its centre lies behind the reflector and nearer to it than the centre of the incident system.

These phenomena, which can be observed directly in the case of water waves, occur also for all wave motions. A more exact mathematical treatment of them follows in § 5, p. 239 *et seq.*

7. Progressive Waves.—The direct observation of waves on the surface of water gives the impression of a forward motion, although the individual water particles only perform oscillations about an equilibrium position. It is this apparent translational motion which is referred to when we speak of **progressive** or **advancing waves**.

An advancing wave is always formed when each of a succession of particles oscillates according to the same law, but in such a way that there is a constant phase difference between each particle and the next.

2. The Laws of Progressive Transverse Sine Waves.

1. Formation of a Transverse Sine Wave.—If the individual particles of a body perform harmonic vibrations, and if the transmission of

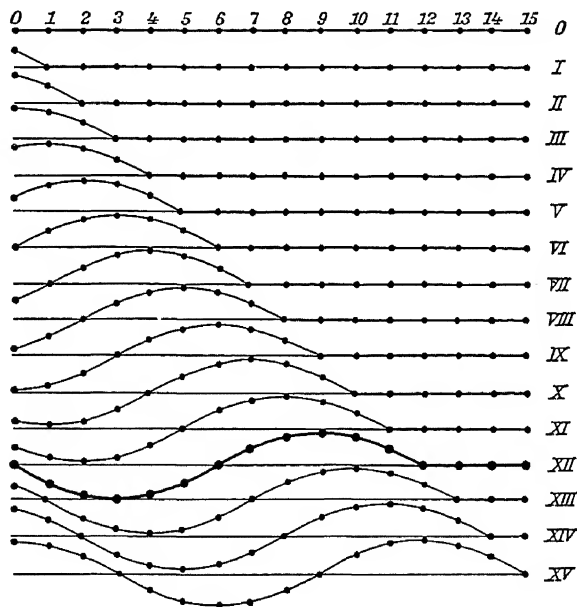


Fig. 15.—Formation of an Advancing Transverse Wave

energy from one particle to the next is at right angles to their direction of vibration, we obtain the result shown in fig. 15. The displacements of the particles are shown after fifteen successive equal intervals of time, the phase change in each interval being $\pi/6$ (see subsection 2, immediately following; reference may also be made to the section on simple harmonic motion, Vol. I, p. 146).

Each particle begins its motion one interval of time after the particle before it. In the figure it has been assumed that the zero

particle is once more passing through its initial position with the initial velocity in the initial direction when the twelfth particle is just beginning to move. This moment corresponds to the curve XII of fig. 15. The phase difference between successive particles is thus $\pi/6$.

The distance from any particle to the next particle in the same state of motion is called the **wave-length**. The maximum displacement is called the **amplitude** of the wave (p. 209). This kind of wave is said to be **transverse**, since the direction of vibration of each particle is at right angles to the direction of advance of the wave itself.

2. The Wave Equation.—According to p. 146, Vol. I, the law governing the transverse harmonic motion of each particle is expressible by the equation

$$y = r \sin \varphi,$$

where y is the displacement, i.e. the ordinate of the particle in fig. 15, r the amplitude and φ the angle determining the corresponding time. This angle is called the **phase angle**. The time T required by each particle for a complete oscillation is called the **period**. During one complete period φ passes through all values from 0 to 2π ; hence φ changes by $2\pi/T$ per unit of time. The value of φ corresponding to any time t is therefore $\varphi = (2\pi/T)t$. Hence the law of harmonic motion can also be written in the form

$$y = r \sin \left(\frac{2\pi}{T} t \right).$$

This involves the assumption that the motion of the particle begins at the time $t = 0$. It holds therefore for the zero-particle.

The first particle does not begin its motion until a certain time θ (in our case $\frac{1}{12}T$) has elapsed. The equation of its motion is therefore

$$y_1 = r \sin \left[\frac{2\pi}{T} (t - \theta) \right].$$

For the p th particle we have similarly

$$y_p = r \sin \left[\frac{2\pi}{T} (t - p\theta) \right].$$

If we consider n particles (in our case 12) to the wave-length, we have $n\theta = T$ or $\theta = T/n$. In this case the equation of motion for the p th particle is

$$y_p = r \sin \left[\frac{2\pi}{T} \left(t - \frac{p}{n} T \right) \right].$$

Let the wave-length, i.e. the distance between the zero and the n th particle, be λ . Further let the distance of the p th particle from the zero particle be x . Then

$$x : \lambda = p : n,$$

and therefore, finally,

$$y_p = y_x = r \sin \left[\frac{2\pi}{T} \left(t - \frac{x}{\lambda} T \right) \right]$$

or

$$y_x = r \sin \left[2\pi \left(\frac{t}{T} - \frac{x}{\lambda} \right) \right].$$

This is the equation of motion of any particle of the wave.

The equation contains the two variables t and x . If we wish to derive from it the equation of motion of a *selected particle*, we consider x as a constant. The equation then simplifies to

$$y = r \sin \left[2\pi \left(\frac{t}{T} - C \right) \right].$$

If, on the other hand, the equation is to express the displacement of all the points at a *selected time*, we must keep t constant. The equation then simplifies to

$$y = r \sin \left[2\pi \left(C' - \frac{x}{\lambda} \right) \right].$$

A comparison of the last two equations confirms what is at once clear from the geometrical derivation of the wave, namely, that it makes no difference to the investigation whether we consider the successive states of motion of a selected point or the simultaneous states of motion of all the points at a selected time. In other words:

The cinematographic picture of the motion of a selected point of a transverse wave is identical with the instantaneous picture of the whole wave.

3. Energy of a Wave.—Differentiating the wave equation with respect to t we obtain the velocity of any oscillating point ($x = \text{const.}$), viz.,

$$v_x = \frac{dy}{dt} = \frac{2\pi r}{T} \cos \left[2\pi \left(\frac{t}{T} - \frac{x}{\lambda} \right) \right].$$

In the same way for the acceleration we obtain

$$a_x = \frac{dv_x}{dt} = -\frac{4\pi^2 r}{T^2} \sin \left[2\pi \left(\frac{t}{T} - \frac{x}{\lambda} \right) \right] = -\frac{4\pi^2}{T^2} y_x.$$

If the mass of the oscillating particle is m , its kinetic energy is

$$\frac{1}{2} m v_x^2 = \frac{2m\pi^2 r^2}{T^2} \cos^2 \left[2\pi \left(\frac{t}{T} - \frac{x}{\lambda} \right) \right]$$

and its potential energy

$$-\int_0^y m a_x dy_x = +\frac{4m\pi^2}{T^2} \int_0^{y_x} y_x dy_x = \frac{2m\pi^2}{T^2} y_x^2 = \frac{2m\pi^2 r^2}{T^2} \sin^2 \left[2\pi \left(\frac{t}{T} - \frac{x}{\lambda} \right) \right].$$

The total energy of the particle is therefore

$$E = \frac{2m\pi^2 r^2}{T^2} \left\{ \cos^2 \left[2\pi \left(\frac{t}{T} - \frac{x}{\lambda} \right) \right] + \sin^2 \left[2\pi \left(\frac{t}{T} - \frac{x}{\lambda} \right) \right] \right\} = \frac{2m\pi^2 r^2}{T^2}.$$

Hence also in the case of a wave:

The energy is proportional directly to the square of the amplitude and to the mass of the oscillating particles and inversely to the square of their period of oscillation.

Every particle in a wave train has the same energy, provided that the amplitude and masses of the particles remain constant throughout.

4. Components of a Wave and their Superposition.—The displacements y , the velocities v , and the accelerations a of the oscillating points are vector quantities and as such may be resolved into components by the parallelogram law. Thus a transverse wave may be resolved into component waves whose displacements, velocities and accelerations are the components of the respective quantities in the original wave. The component waves can be treated as separate individuals, each governed by the laws of wave motion. Conversely several waves can be combined according to the parallelogram law to give one resultant wave.

5. Relationship between Velocity of Propagation, Frequency, and Wave-length.—If we wish to find out which points of a wave train have the same displacement y_x , velocity v_x and acceleration a_x , we must keep the phase angle constant. All points x having exactly the same displacement, velocity and acceleration are therefore given by

$$2\pi\left(\frac{t}{T} - \frac{x}{\lambda}\right) = \text{const.}$$

Taking the special case in which the displacement considered is that of the point $x = 0$ at the time $t = 0$, we have

$$\frac{t}{T} - \frac{x}{\lambda} = 0 \quad \text{or} \quad \frac{x}{t} = \frac{\lambda}{T} = c.$$

That is to say, all the points have the same displacement in succession, this equivalence of phase advancing with velocity x/t along the wave

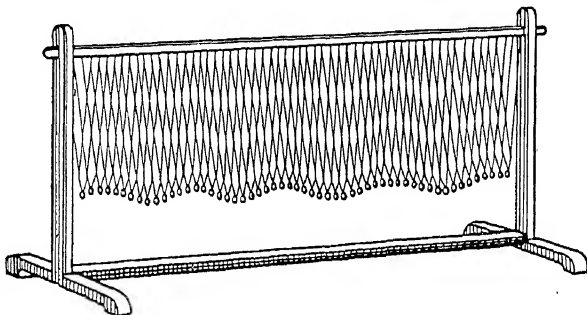


Fig. 16.—Wave in a Series of Coupled Oscillating Points

train. The velocity c is called the **velocity of propagation** of the wave or the **wave velocity**. Calling $1/T = \nu$ the **frequency*** of the wave, we have

$$c = \nu\lambda.$$

This equation can also be derived easily in a more direct way. During each complete oscillation of a particle the wave advances by one wave-length λ . Hence if each particle performs ν oscillations per second, the wave must advance a distance $\nu\lambda$ in a second. But this is the velocity of propagation c .

6. Group Velocity.—The above simple considerations only hold so long as the velocity of propagation of the wave is independent of the wave-length. If this is not the case, the conditions are much more complicated. An experiment may serve to convince us that under certain conditions not infrequently met with in nature it is necessary in dealing with wave-motion to distinguish between different velocities.

We make use of a net loaded with a row of lead balls as shown in fig. 16. We move one end of this once or oftener backwards and forwards in a transverse

* The frequency is sometimes defined as the numerical value of $2\pi/T = 2\pi\nu$, i.e. the number of oscillations in 2π seconds.

direction and then hold it still. The disturbance travels along the row of lead balls in a different manner from that previously described. If we watch one of the advancing crests carefully, we see that its amplitude becomes smaller and smaller as its distance from the initial point of disturbance increases, until finally it vanishes altogether. But new waves follow behind the vanishing wave and behave in the same manner. Before dying out, however, each one of these waves gets farther in the direction of its motion than the one before it. Any given lead ball of the row therefore swings with initially increasing amplitude. It is seen that the original disturbance distributes itself over a certain length of the row. Within this length we can recognize a number of waves following one another: we have what is called a "wave group" with a definite beginning and a definite end. This group moves forward with a smaller velocity than that of the waves within it. These waves are formed anew at the rear of the group, move along it, decrease in amplitude and finally disappear at its "head". It is not difficult to determine experimentally the time which the disturbance takes to travel the length of the net. By dividing the distance by the time we can then obtain the velocity of propagation of the wave group or the **group velocity** as it is called.

We now modify the above experiment by moving the end of the net continuously backwards and forwards instead of holding it still after a few oscillations. The wave train now produced has no end. Its head moves right across the net, is reflected at the far end and moves back again to the initial point of disturbance. In this way stationary waves are formed as explained in § 4, p. 232 *et seq.* From this moment onwards the phenomenon of a special group velocity is no longer perceptible in the motion of the net. Instead we have two wave trains moving in opposite directions with constant amplitude. Their phases are propagated with a constant velocity greater than the group velocity. This wave velocity c can be determined from the period T and the wave-length λ ($\lambda = cT$).

The reason for this peculiar behaviour of waves at the loaded edge of the net is to be found in the fact that the lead balls have a certain *natural period*. Each ball can be regarded as the bob of a pendulum suspended from the cross beam carrying the net. Each of these pendulums is coupled to its neighbours and tends to swing with its natural period. A more accurate theoretical investigation shows that oscillations of different frequencies are propagated with different wave velocities; the less the period differs from the natural period of the pendulums, the greater the wave velocity. For the calculation of group velocity see subsection 10 below. It may be mentioned that in the case of water waves the wave velocity also depends in general upon the wave-length (p. 211), and that therefore the waves within a wave group (e.g. the groups produced by individual drops falling into a deep basin of water) show a behaviour similar to that described above for the loaded net.

7. Superposition of Waves.—Component waves do not affect each other, but combine to give one resultant wave whose displacement at any point is obtained by the addition of the corresponding component displacements. Thus each particle of the medium through which the wave is propagated may perform a number of oscillations simultaneously.

Conversely **Fourier's* theorem** states that *every wave motion*, no matter what the form of the advancing disturbance, *can be represented as the superposition of component sine waves of different wave-length*. The mathematical equation expressing this theorem is

$$y_x = f(x - ct) = r_1 \sin 2\pi \left(\frac{x - ct}{\lambda_1} + \delta_1 \right) + r_2 \sin 2\pi \left(\frac{x - ct}{\lambda_2} + \delta_2 \right) + \dots$$

* J. B. J. FOURIER (1768–1830), Paris.

or more shortly

$$y_x = f(x - ct) = \sum_{\lambda} r_{\lambda} \sin 2\pi \left(\frac{x - ct}{\lambda} + \delta_{\lambda} \right).$$

The summation extends over a number of terms each corresponding to a different value of λ , and hence also of the amplitude r and the phase difference δ . The values of r and δ in the components vary according to the form of the original wave, i.e. according to the nature of the function f . In most practical cases f is a periodic function. In this case it is possible to find the component of greatest period and to express the periods of the remaining components as integral fractions of this *fundamental*.

The mathematical expression of Fourier's theorem then assumes the somewhat simpler form

$$y_x = \sum_{(n)} \left[a_n \sin \frac{2\pi n}{\lambda} (x - ct) + b_n \cos \frac{2\pi n}{\lambda} (x - ct) \right].$$

The summation is now to be performed over all the values of the term in the square brackets corresponding to integral values of n from 0 to ∞ . The coefficients a_n and b_n are the amplitudes of the components. Their values can be calculated by special methods given by FOURIER, provided that the form of the resultant wave motion, i.e. the function f , be known. The process of determining the amplitudes of the components of a given wave form, whether by mathematical or experimental methods, is called **harmonic analysis**.

8. Dispersion.—In the case of a wave disturbance in a medium in which the velocity of propagation varies with the wave-length (as, for example, in the net apparatus of fig. 16, p. 222), the different components have different velocities. After a while, therefore, they become separated. The form of the wave cannot remain constant, as it does when the components all have the same velocity. We say that there is a **dispersion** of the components. *Dispersion always occurs in a row of points possessing a natural period, or (more generally) in a medium consisting of such points.*

9. Beats.—If we superimpose two wave trains of equal amplitude r and wave velocity c but different periods and hence also different frequencies ν and ν_1 , then in accordance with the above, the resultant displacement is given by

$$\begin{aligned} Y_x &= r \sin \left[2\pi \nu \left(t - \frac{x}{c} \right) \right] + r \sin \left[2\pi \nu_1 \left(t - \frac{x}{c} \right) \right] \\ &= 2r \cos \left[2\pi \left(t - \frac{x}{c} \right) \left(\frac{\nu - \nu_1}{2} \right) \right] \sin \left[2\pi \left(t - \frac{x}{c} \right) \left(\frac{\nu + \nu_1}{2} \right) \right] \end{aligned}$$

If in addition ν and ν_1 differ only slightly from one another, so that $\nu - \nu_1 = \Delta\nu$ is a small quantity, the equation assumes the approximate form

$$Y_x = 2r \cos \left[\frac{2\pi \Delta\nu}{2} \left(t - \frac{x}{c} \right) \right] \sin \left[2\pi \nu \left(t - \frac{x}{c} \right) \right].$$

This can be interpreted by regarding it as the equation of a single harmonic wave of frequency ν and of amplitude

$$2r \cos \left[\frac{2\pi \Delta\nu}{2} \left(t - \frac{x}{c} \right) \right].$$

Thus the amplitude is itself a periodically variable function. Its maximum value of $+2r$ and its minimum value of $-2r$ are each assumed $\Delta\nu/2$ times per second. Neglecting the sign, we can say that the displacement varies $\Delta\nu$ times per second between the values zero and $2r$. At any selected point for which

$x = \text{const.}$ the motion of oscillation therefore vanishes and appears again Δv times per second. The amplitude is at first vanishingly small, then works up to the value $2r$ and subsequently dies down again to zero, whereupon the process is repeated anew. These rhythmical increases and decreases of the energy of oscillation are the beats of the two superimposed wave trains (cf. fig. 8, p. 195). We have thus confirmed the result already enunciated above:

The number of beats per second is equal to the difference between the frequencies of the two superimposed wave trains.

We will now consider the succession of points in the wave, i.e. we will take x as variable. In this way we see the different values of the amplitude side by side in space, instead of one after another in time as is the case when $x = \text{const.}$ Now all points x satisfying the equation

$$t - \frac{x}{c} = \text{const.},$$

for example

$$t - \frac{x}{c} = 0 \quad \text{or} \quad \frac{x}{c} = t,$$

have the same amplitude. A given value of the amplitude thus moves along with the wave velocity c . The infinitely long wave train is subdivided into sections by the points of zero amplitude. These are given by

$$2\pi\Delta v \left(t - \frac{x}{c} \right) = (2n + 1) \frac{\pi}{2}$$

where n is a whole number. At a given moment, e.g. $t = 0$, we have from the last equation

$$x = - (2n + 1) \frac{c}{2\Delta v},$$

that is to say, successive points of zero amplitude are separated by a distance equal to $c/\Delta v$. The whole wave motion is therefore made up of elementary wave trains of length $c/\Delta v$, which follow one another with the same velocity c (see figs. 9 and 10, p. 195).

10. Quantitative Expression for the Group Velocity.—We can generalize the above case by assuming that the wave velocity is different for the different frequencies v and v_1 . This is the case of beats in a medium showing *dispersion*. The two superimposed wave trains then satisfy the equation

$$Y_x = r \sin \left[2\pi \left(\frac{ct - x}{\lambda} \right) \right] + r \sin \left[2\pi \left(\frac{c_1 t - x}{\lambda_1} \right) \right]$$

in which c and λ refer to the wave of frequency v and c_1 and λ_1 to the wave of frequency v_1 . We may regard $c - c_1 = \Delta c$ and $\lambda - \lambda_1 = \Delta \lambda$ as small quantities. Transforming the sum on the right-hand side into a product as before, we obtain

$$Y_x = 2r \cos \left[\frac{2\pi}{2} \left\{ t \left(\frac{c}{\lambda} - \frac{c_1}{\lambda_1} \right) - x \left(\frac{1}{\lambda} - \frac{1}{\lambda_1} \right) \right\} \right] \sin \left[\frac{2\pi}{2} \left\{ t \left(\frac{c}{\lambda} + \frac{c_1}{\lambda_1} \right) - x \left(\frac{1}{\lambda} + \frac{1}{\lambda_1} \right) \right\} \right].$$

Remembering that Δc and $\Delta \lambda$ are small quantities, we may write

$$Y_x = 2r \cos \left[\frac{2\pi}{2} \left\{ \left(\frac{\lambda \Delta c - c \Delta \lambda}{\lambda^2} \right) t + \frac{\Delta \lambda}{\lambda^2} x \right\} \right] \sin \left[2\pi \left(\frac{ct - x}{\lambda} \right) \right].$$

Interpreting this in the same way as in the previous treatment, we see that it represents an infinitely long wave train of wave-length λ , whose waves move with the *wave velocity* c and whose amplitude again varies periodically with the time and with the abscissa x .

The points of zero amplitude divide up the infinite wave train into elementary wave groups of equal length. The velocity of motion of these groups, however, is no longer the same as the wave velocity (see p. 223). We find its value c' , as in the foregoing treatment of beats, by putting the angle of the cosine function equal to zero and solving for the quotient x/t . This gives

$$(\lambda \Delta c - c \Delta \lambda)t + x \Delta \lambda = 0$$

$$\text{i.e.} \quad \frac{x}{t} = c' = c - \lambda \frac{\Delta c}{\Delta \lambda}.$$

For vanishingly small $\Delta \lambda$ and Δc the equation becomes

$$c' = c - \lambda \frac{dc}{d\lambda} \quad (\text{Rayleigh's * equation}).$$

This equation shows how the **group velocity** c' can be calculated when the relationship between the *wave velocity* c and the wave-length is known. It teaches further that with vanishing wave-length the group velocity becomes equal to the wave velocity (p. 223). If the *dispersion* of the medium is such that the wave velocity increases with increasing wave-length, then $\frac{dc}{d\lambda}$ is positive and the group velocity is smaller than the wave velocity. Within a wave group between two successive points of zero amplitude the waves therefore move from the rear of the group to its head, their amplitudes at first increasing and then decreasing again (p. 223).

11. Propagation of Energy in a Wave Train.—In an advancing wave train new waves are continually being formed at the head, e.g. at the far end of a long rope whose near end is being moved backwards and forwards harmonically. Thus energy is propagated along the train; the energy of the new motion appearing at its head is supplied from behind. In such an advancing wave train a new length c is set in motion every second. Hence the energy transmitted must be equal to the energy of a single oscillating particle multiplied by the number of such particles in the length c . If each particle is of mass m , length Δx , cross-section a and density s , we have $m = as \Delta x$ and the number of such particles in the length c is $c/\Delta x$. Hence the amount of energy passing through the cross-section a per second (see p. 221) is

$$\frac{c}{\Delta x} E = \frac{2\pi^2 r^2}{T^2} as \Delta x \cdot \frac{c}{\Delta x} = 2\pi^2 r^2 v^2 cas.$$

In cases when it is necessary to distinguish between *wave velocity* and *group velocity*, the quantity c in this equation is the *group velocity*. Such a propagation (or radiation) of energy also occurs when the energy is continually converted into heat by resistance at one end of the wave train, so that a damping of the wave motion would occur if new energy were not continually supplied. We shall become acquainted in Mach's wave apparatus (fig. 23, p. 239) with a device by means of which waves can be produced in a row of points not coupled together in any way. There is, of course, no propagation of energy in a wave of this kind. Similarly in the case of a wave train in a row of very loosely coupled points

* JOHN WILLIAM STRUTT, third BARON RAYLEIGH (1842-1919), Cavendish Professor of Experimental Physics in the University of Cambridge from 1879 to 1884, and Professor of Natural Philosophy at the Royal Institution of Great Britain from 1887 to 1905. The first observations upon the difference between group velocity and wave velocity were made by the brothers WEBER (WILH. ED., 1804-91, ERNST HEINR., 1795-1878) at Göttingen (p. 208).

possessing a natural period the velocity of propagation of energy must be considered smaller than the wave velocity.

12. Investigation of the Velocity of Propagation of Transverse Waves in Stretched Strings.—The velocity with which a transverse wave moves along a stretched string depends upon the tension of the string, its thickness and the density of the material of which it is made. The nature of this dependence can be determined in the following way. A steel wire of about 0.9 mm. diameter and about 60 m. long is stretched between the ends of a long corridor as shown in fig. 17. The one end of the wire is fastened directly to the wall, while between the other end and the other wall are introduced a spring balance and a pulley block. In order to mark off a definite length, pieces of wood with sharp upper edges are placed as props beneath the wire near its two ends. By means of the pulley block the wire can be stretched with any desired tension, the value of which is read off on the spring balance. The wire is given a sharp blow near one of the props. The disturbance so produced moves along to the opposite end, where it is reflected with reversal of phase and passes back again. It is reflected again at the first end and thus moves backwards and forwards along the wire several times. The number of such complete journeys along the wire in a given time is noted, and from it the velocity of propagation is calculated.

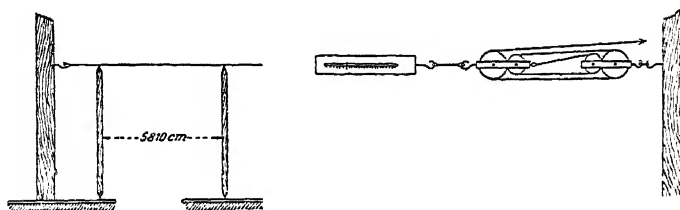


Fig. 17.—Velocity of Propagation of a Wave along a Stretched Wire

An observation upon a steel wire 58.10 m. long and 0.9 mm. thick at a tension of 5 kg. wt. gave the result that the wave covered the length of the wire 100 times in a minute. Thus the distance moved by the wave per minute was 5810 m. or per second approximately 100 m.

When the tension of the string is increased to four times or nine times its original value, the velocity of propagation of the wave is doubled or trebled respectively. Hence:

The velocity of propagation of a wave along a string is proportional to the square root of the tension.

If a steel wire of double the thickness, i.e. of four times the cross-sectional area, is used, the velocity of propagation is halved. From a large number of similar observations upon steel wires of different thicknesses it follows that:

The velocity of propagation of a wave along a string is inversely proportional to the diameter of the string, i.e. inversely proportional to the square root of its cross-sectional area.

Finally, investigations upon strings of other materials (i.e. with other densities) show that:

The velocity of propagation is inversely proportional to the square root of the density of the substance of which the string is made.

We can combine the last two results as follows:

The velocity of propagation is inversely proportional to the square root of the mass per unit length of the string.

It is usual to express these relationships in terms of the frequency ν of the string, i.e. the number of backward and forward oscillations of the transverse

wave per second, instead of in terms of the velocity of propagation. The experimental results can then be summed up by means of the formula *

$$v = \frac{1}{2l} \sqrt{\frac{p}{d}}$$

where v is the frequency, l the length of the string, p the tension, and d the mass per unit length. All these quantities are to be expressed in C.G.S. units.

3. Progressive Longitudinal Sine Waves

1. **Formation of a Longitudinal Sine Wave.**—When the individual particles of a body perform harmonic vibrations and when the energy

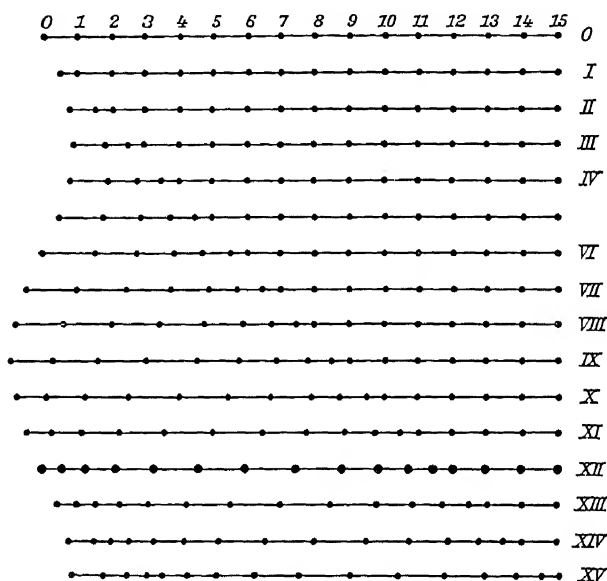


Fig. 18.—Formation of Longitudinal Waves

transmission from one to the next is in the same direction as the vibration, the particles periodically approach and recede from one another: alternate compressions and rarefactions occur in the body. Fig. 18 shows fifteen stages (separated by equal intervals of time) in the formation and course of such a longitudinal wave.

The simplest way of constructing a longitudinal wave is that shown in fig. 19. This consists of drawing a transverse wave and then turning each displacement through 90° , an upward displacement of the transverse wave becoming a dis-

* The laws expressed in this equation were first established in a purely experimental manner by MERSENNE (about 1633). The formula itself was later (1715) derived mathematically by B. TAYLOR (1685–1731, English mathematician). It does not give exact values, especially for rapid vibrations, because it takes no account of the natural “stiffness” of the string, which is equivalent to a tension. The formula only holds for the ideal case of a perfectly flexible string, devoid of all flexural rigidity.

placement to the right in the longitudinal wave and a downward displacement becoming a displacement to the left. Taking account of the direction of propagation of the transverse and longitudinal waves as well as that of the motion of the individual particles, we see at once from the figure that:

At the compressions the particles move in the same sense as the whole wave, at the rarefactions in the opposite sense.

Longitudinal waves are mostly maintained by the action of elastic forces. The energy transmission from one particle to the next then occurs in exactly the same way as was discussed in Vol. I, p. 217 *et seq.*

2. Velocity of Propagation of Elastic Longitudinal Waves.—This is the same as the velocity c of propagation of an impulse imparted to one end of an

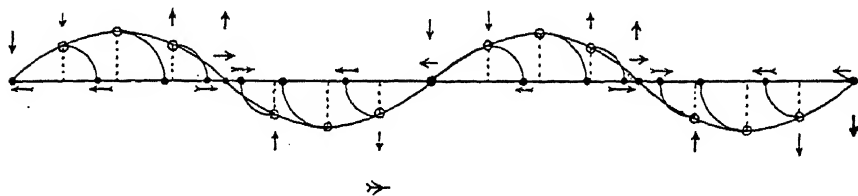


Fig. 19.—Relation between Transverse and Longitudinal Waves

elastic rod, which was derived in the passage just cited from Young's modulus E and the density ρ . All the quantities being expressed in C.G.S. units, we have

$$c = \sqrt{\frac{E}{\rho}}$$

From this we can calculate, for example, the velocity of propagation of a longitudinal wave in a steel wire. Here $E_1 = 21,000$ kg. wt./mm.² whence

$$E = 21,000 \cdot 1000 \cdot 100 \cdot 981 \text{ dynes/cm.}^2 = 2.06 \cdot 10^{12} \text{ dynes/cm.}^2;$$

and $\rho = 8.0$ gm./cm.³ (see also Vol. I, p. 219).

Hence

$$c = \sqrt{\frac{2.06 \cdot 10^{12}}{8.0}} \text{ cm. per sec.} = 5100 \text{ m. per sec.}$$

The velocity of propagation is independent of the amplitude and the frequency, provided that the deformations follow the simple Hooke's law, i.e. are proportional to the stresses.

In order to be able to calculate the velocity of propagation of a *longitudinal wave in a column of air* by the same formula, we must know the modulus of elasticity of the air. Imagine a volume V cm.³ of a gas enclosed under the pressure p dynes/cm.² in a cylinder of length l cm. and cross-sectional area A fitted with a movable piston. Then $V = lA$. The column of gas may be compared to a wire which can be stretched or compressed by an applied force. If the piston is driven in with the additional thrust $\Delta P = A\Delta p$, the gas column is shortened by the amount Δl and its volume thus diminished by the amount $\Delta V = A\Delta l$. We can apply Hooke's law to this process, provided that the formula given (Vol. I, p. 197) is suitably modified. The force P in this formula now becomes $\Delta P = A\Delta p$. Similarly the extension $l' - l$ becomes $-\Delta l$, because formerly an increase of length accompanied an increase of force, whereas now the reverse is true. Further, the modulus of elasticity E_1 was formerly expressed in kg. wt./mm.², whereas

we must now express all the quantities in C.G.S. units. Hence Hooke's law, which was previously expressed in the form (Vol. I, p. 197)

$$P = EA \cdot \frac{l' - l}{l}$$

now becomes

$$\Delta P = -E'A \frac{\Delta l}{l},$$

whence

$$E' = -\frac{\Delta P}{A} \cdot \frac{l}{\Delta l}.$$

Substituting $\Delta P/A = \Delta p$ and remembering that

$$\frac{l}{\Delta l} = \frac{Al}{A\Delta l} = \frac{V}{\Delta V},$$

we obtain for the (bulk) modulus of elasticity of the gas

$$E' = -\Delta p \frac{V}{\Delta V} = -V \frac{\Delta p}{\Delta V}.$$

Within the elastic limits the elastic extension of a wire is proportional to the stress. It is also so small in comparison with the total length that the latter can be taken as constant in applying Hooke's law. In the case of gases, therefore, Hooke's law can only be applied for very small volume changes and very small forces; otherwise the volume V , which appears as a factor, cannot be regarded as constant. *With this assumption* we can replace the difference quotient $\Delta p/\Delta V$ by the differential coefficient $\frac{dp}{dV}$. We then obtain the expression

$$E' = -V \frac{dp}{dV}$$

for the (bulk) modulus of elasticity of a gas (and naturally also of a liquid).

Substituting this in the formula for the velocity of propagation of a longitudinal wave, we have

$$c = \sqrt{\frac{E'}{\rho}} = \sqrt{-\frac{V}{\rho} \frac{dp}{dV}}.$$

The *relative expansion* due to the increase of pressure dp is $-dV/V$. The corresponding value for unit increase of pressure is therefore

$$-\frac{1}{V} \frac{dV}{dp}$$

and is called the *compressibility*. The reciprocal of the compressibility is the *modulus of elasticity or volume elasticity* of the gas (or liquid).

I. On the assumption that the propagation of a longitudinal wave in a gas is an *isothermal* process, we may put $pV = \text{const.}$ (Boyle's law, Vol. I). Differentiating this equation, we obtain

$$Vdp + p dV = 0,$$

whence

$$-V \frac{dp}{dV} = p.$$

Substituting this in the expression for c we have

$$c = \sqrt{\frac{p}{\rho}} \quad (\text{Newton's formula, 1686}).$$

For ordinary air, $p = 76 \cdot 13 \cdot 6 \cdot 981$ dynes/cm.², $\rho = 0.001293$ gm./cm.³,

and hence $c = \sqrt{\frac{76 \cdot 13 \cdot 6 \cdot 981}{0.001293}}$ cm. per sec. = 280 m. per sec.

This value is quite out of agreement, however, with the observed velocity of propagation of a longitudinal wave in air.

II. On the assumption that the propagation of a longitudinal wave in a gas is an *adiabatic* process, we must make use of Poisson's law, namely, $pV^\gamma = \text{const.}$ (p. 95). Differentiating this equation we obtain

$$V^\gamma dp + p\gamma V^{\gamma-1} dV = 0,$$

whence
$$-V \frac{dp}{dV} = \gamma p.$$

Substituting this in the expression for c , we have

$$c = \sqrt{\frac{\gamma p}{\rho}} \quad (\text{Laplace's equation, 1816}).$$

From this we can calculate the velocity of propagation of a longitudinal wave in air by putting $p = 76 \cdot 13 \cdot 6 \cdot 981$ dynes/cm.², $\rho = 0.001293$ gm./cm.³ and $\gamma = 1.4$. This gives

$$c = \sqrt{\frac{76 \cdot 13 \cdot 6 \cdot 981 \cdot 1.4}{0.001293}} \text{ cm. per sec.} = 331.3 \text{ m. per sec.}$$

Certain elastic longitudinal waves are perceptible to us as sound. Thus the above is the velocity of sound in air. After taking careful account of all the conditions the mean of many thousands of observations made during the Great War by German and also by French sound-ranging corps comes out to $c = 330.8$ m. per sec. at 0° C. (At 15° C. the value is 339.8 m. per sec.) The small but appreciable variation from the calculated result remains unexplained.* Hence the propagation of sound must be regarded as an adiabatic process. In actual fact the time between successive compressions and rarefactions of the air during the passage of sound is so small that a temperature equalization between neighbouring regions does not occur.

From the observation of c it is possible to determine γ , the ratio of the two specific heats of a gas, and thus to decide whether its molecules contain one, two, three or more atoms. This is indeed the way in which the monatomic nature of the noble gases was first established, since chemical methods are inapplicable on account of the inertness of these substances. If the velocity of sound is measured with Kundt's tube by the method developed on p. 265, only quite small quantities of gas are required.

The equation
$$c = \sqrt{-\frac{V}{\rho} \frac{dp}{dV}}$$

also holds for the propagation of longitudinal waves in *liquids*. From the observed value of 1435 m. per sec. in water (first determined in 1827 by COLLADON and STURM in the Lake of Geneva) we obtain the value $0.0000476 \approx 1/21,000$ for the compressibility of water (per atmosphere). This is in good agreement with the results of measurements by other methods (p. 268, Vol. I).

* According to determinations made by the German Physikalisch-Technische Reichsanstalt the value for dry air free from carbon dioxide is $c_0 = 331.57$ m. per second. From this we obtain $\gamma = 1.403_4$. For hydrogen the value $c_0 = 120.6$ m. per sec. was found. From this $\gamma = 1.408$.

3. Comparison of the Velocities of Propagation of Elastic Longitudinal and Transverse Waves.—The fundamental formula for the velocity of propagation of elastic waves (thermal effects being neglected) is

$$c = \sqrt{\frac{E'}{\rho}}.$$

In this formula the particular value to be taken for the elastic constant E' depends on the type of wave which we are considering.* Liquids and gases have no rigidity and consequently there can be no transverse but only longitudinal elastic waves. (Waves of this kind must not be confused with the waves on the surface of a liquid; these are not due to elastic forces.) In solids both longitudinal and transverse waves are possible; both are indeed produced by a disturbance in the interior of a solid body. The velocity of propagation of longitudinal waves is greater than that of transverse waves.

Observations upon elastic waves are of importance for the investigation of the interior of the earth. Thus from the velocity of earthquake waves it is possible to draw conclusions as to the density and elasticity of the earth's interior. In the upper layers the mean value of c for longitudinal waves is from 4 to 6 km. per sec. Since this value varies according to the nature of the rocks, attempts have been made to use measurements upon elastic waves for the purpose of locating deposits of ore.

4. Stationary Waves

1. Transverse Waves.—Up to the present we have assumed that the media in which the waves are propagated are of unlimited extent. This does not correspond to actual fact. At the edges of a vessel of water or at the ends of a stretched string new effects are produced which considerably alter the phenomena.

It was shown on p. 227 that a single disturbance in a stretched string is reflected at the end, there being no phase change when the end is free and a reversal of phase when it is fixed. This reflection of the individual disturbances also takes place when a train of advancing waves reaches the end of the string. It follows, therefore, that after reflection every point of the string lying within the reflected wave is under the simultaneous influence of two waves moving in opposite directions—the incident wave and the reflected wave.

When a particle performs two motions simultaneously, they are added together. If the component motions are in the same or in opposite directions, the addition is algebraic; if they are inclined to one another, the addition is according to the parallelogram law. Thus the velocity of a point in presence of two waves is the geometrical sum of the velocities which it would have in the presence of either of the two waves alone. The same applies also to its displacement. The maximum displacement in the case of a sine wave is the amplitude. Hence when two

* For longitudinal waves in a cylindrical bar E' is Young's modulus; for waves of simple distortion (transverse waves in an infinite solid) E' is the modulus of rigidity n ; for longitudinal (sound) waves in an infinite fluid E' is the bulk modulus k ; for longitudinal (sound) waves in an infinite solid E' is $k + \frac{4}{3}n$. (See Vol. I, Appendix I, p. 408.)

independent wave trains cross one another, their amplitudes add together geometrically (principle of the superposition of waves, pp. 211, 221 and 223). In our case of purely transverse waves in a string each particle performs two simultaneous motions at right angles to the string, i.e. in the same or opposite directions. Hence at any moment

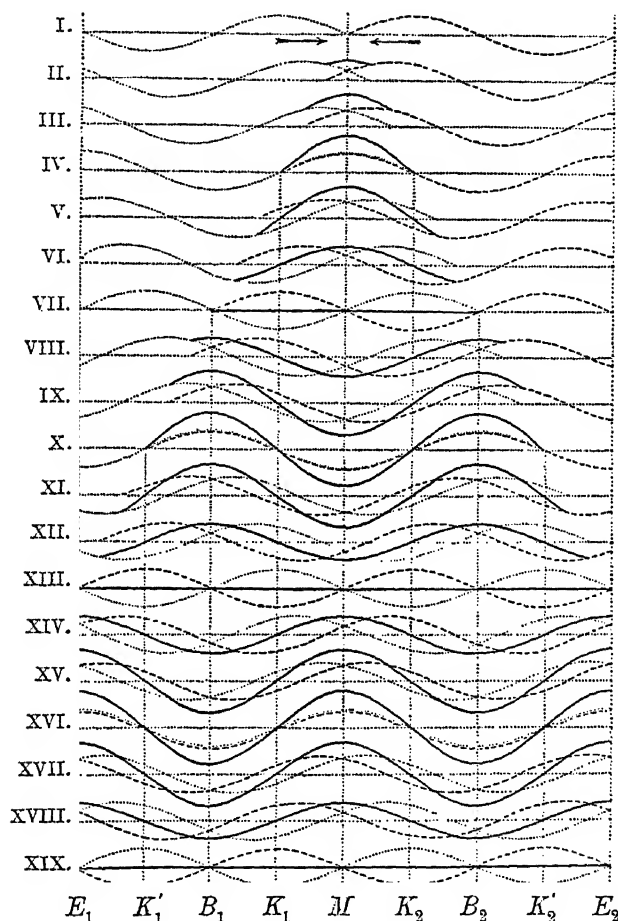


Fig. 20.—Formation of Stationary Waves

the displacement of any point of the string taking part in both motions is obtained by algebraic addition of the corresponding component displacements.

Fig. 20 shows 19 stages in the effect produced when two exactly similar transverse waves meet upon the same string. The wave moving from left to right is shown as a dotted line, the wave moving from right to left as a broken line. The instant at which the two waves meet at the middle of the figure is shown in I. In II the waves have each advanced by $\frac{1}{12}$ of a wave-length. Each successive stage represents a further advance of $\frac{1}{12}$ of a wave-length by each wave. The new

wave found by the algebraic addition of the component displacements is represented by the heavy continuous line. In VII each of the waves has progressed by $\frac{1}{2}$ a wave-length since their meeting. At this stage the component displacements of every point are equal and opposite, so that the total effect is to leave every point in its equilibrium position; the displacements are all zero. The same state is reached again in XIII, XIX, &c.

In IV, X and XVI the middle point M of the string has its maximum displacement towards the same side in both component waves. Thus its resultant displacement is twice as great as in either of the components. The same applies to the points B_1 and B_2 in X and XVI.

These points of maximum displacement are at constant positions upon the string. They are called **loops** or **antinodes**. Special mention must also be made of the points K_1' , K_1 , K_2 , K_2' , &c., whose component displacements are always equal and opposite, so that their resultant displacement is always zero. They are called **nodes**.

Since the points of maximum amplitude, like those of zero amplitude, do not alter their position, the resultant wave is called a **stationary wave**—a name which also describes its appearance.

The wave-length of a stationary wave is equal to that of the component advancing waves producing it. It is equal to the distance from a given node to the next but one or from a given antinode to the next but one.

When we pluck a stretched string whose length corresponds to the distance between the two points K_1 and K_2 , a stationary wave is produced with a node at each end of the string and an antinode in the middle. The wave-length is then twice the length of the string.

If the length of the string corresponds to the distance between the points K_1' and K_2 , we obtain a node at each end and in the middle with two antinodes between. The wave-length is then equal to the length of the string.

If the length of the string corresponds to the distance between the points K_1' and K_2' , we obtain a node at each end and two intermediate ones. Antinodes lie between each node and the next.

In all these cases the string is fixed at both ends. The advancing wave is reflected at the end with reversal of phase. Hence the ends of the string must be nodes.

The case in which the ends are free does not occur for a string. But it can occur for a vibrating rod, which may either be clamped at the ends or in the middle. The points where it is clamped become nodes.

When advancing waves are continually produced at one end of a stretched string or wire, they are reflected at the other end and give rise to stationary waves whose wave-length depends upon the period of the original components. If the second wave is produced at the moment when the first one is reflected from the far end, we get the effect shown in fig. 20 between K_1' and K_2 . But if the second wave is sent out when the first has only got half-way along the string, the second wave will meet the reflected first wave three-quarters of the way along the string with reversed phase, so that the first node is formed here. The faster the succession of waves produced at the end, the nearer the first node will be to the far end of the string. Hence also for a stationary wave:

The frequency is inversely proportional to the wave-length (p. 222).

Difference between Progressive and Stationary Waves.—In a progressive wave all the points have the same amplitude, but their

phases are different. In a stationary wave all the points between two successive nodes have the same phase, but their amplitudes are different. At each node the phase changes by π , i.e. the points on the opposite sides of a node move in opposite directions.

2. Longitudinal Waves.—Longitudinal stationary waves are produced by the superposition of two oppositely directed advancing longitudinal waves, the second of which is usually due to the reflection of the first.

The most convenient method of graphical construction is that shown in fig. 21, namely, by turning the displacements of a stationary transverse wave through 90° . Upward displacements must become displacements to the right and downward displacements must become displacements to the left. It is seen from the figure that the greatest variations of density occur at the nodes (the points always at rest) and that the movement of the particles is from the positions

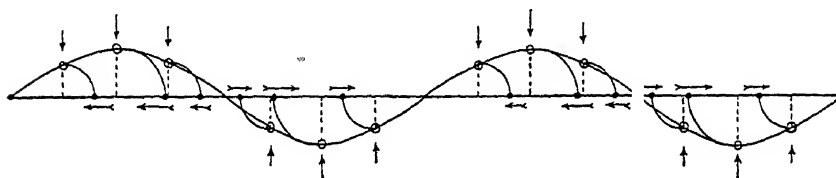


Fig. 21.—Stationary Longitudinal Waves

of maximum density towards the positions of minimum density. Consequently the positions of minimum density become those of maximum density after half an oscillation and vice versa. The antinodes are the points of minimum variation of density.

*The nodes of the motion are therefore the antinodes of the pressure and vice versa.**

When the formation of the stationary waves is due to reflection at a fixed end, this end must be a node on account of the phase reversal on reflection. On the other hand, if the formation of the stationary waves is due to reflection at a free end, this end must be an antinode on account of the similarity of the phases of the incident and reflected waves.

The number of nodes and antinodes formed in a long elastic body depends upon the frequency of the individual particles.

If the ends of an elastic rod are clamped, they must become nodes. In addition, any number of further nodes may be formed at equal distances along the whole length of the rod.

If the ends of the rod are free, they must become antinodes. In addition, any number of alternate nodes and antinodes may be formed at equal distances along the rod.

A rod clamped at one end and free at the other has a node at the former and

* When not otherwise specified, the expressions antinodes and nodes will always be taken, as previously, to refer to the state of *motion*.

an antinode at the latter. Further nodes and antinodes, if any, occur at equal distances along its length.

A column of air enclosed in a tube behaves in exactly the same manner as an elastic rod.

In the case of an elastic rod the longitudinal vibrations are so rapid that they cannot be followed by eye. They can be seen better in the case of a spiral spring. Here it is at least possible to distinguish between nodes and antinodes, because at the nodes, which remain at rest, the coils appear sharp, whereas at the antinodes they appear blurred on account of their rapid backward and forward motion.

Stroboscopic * illumination may be used with advantage for the observation of rapid periodic motions. Fig. 22 shows an arrangement from which the principle

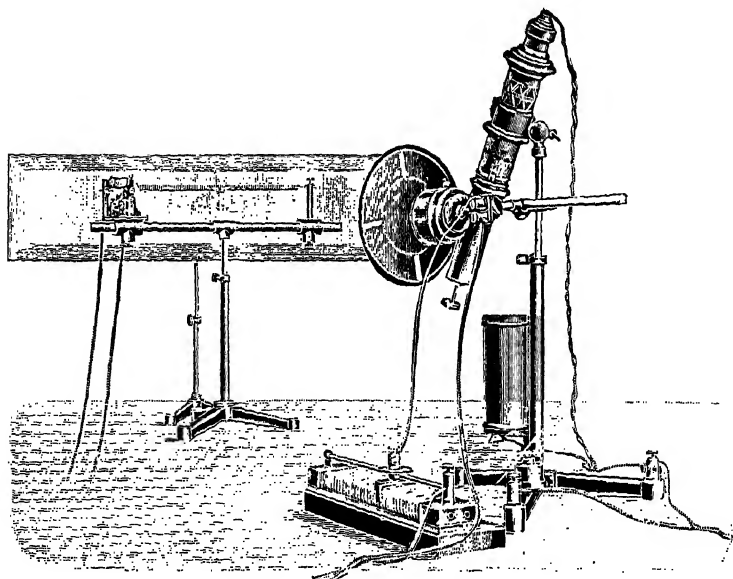


Fig. 22.—Stroboscopic Apparatus

of the method is apparent. In front of a screen is stretched a spiral spring in which stationary longitudinal waves can be set up by an electrical device. The illumination is provided by a small electric arc lamp in front of which a circular disc with several radial slits can be rotated by means of an electromotor. The speed of rotation of the disc can be varied within wide limits by adjustment of a resistance in series with the motor.

When the disc is rotating the beam from the lamp is periodically interrupted. The lamp sends out a flash of light each time a slit passes in front of it.

We will assume that the spiral spring performs 40 longitudinal vibrations per second and that the disc has four slits and revolves 10 times per second, so that 40 flashes fall on the spring every second in regular succession. Then at every flash the spring will be in the same state of motion and will consequently appear to our eyes to be at rest.

If now the speed of revolution of the disc is varied so that there are 39 flashes of light per second, each flash will illuminate the spring when it is in a state of motion $\frac{1}{40}$ of a whole vibration in advance of that illuminated by the preceding flash. During one second, therefore, all the 40 stages of the vibration will be

* Gr., *strobós*, whirl.

illuminated in succession and thus rendered visible. The spring will appear to perform only one vibration per second—a speed which can be followed easily by eye.

Stroboscopic illumination can also be used for the investigation of other periodic processes.

3. Mathematical Treatment of Stationary Waves: Reflection at a Free End.—

We will first consider the case in which the stationary waves are formed by the superposition of two advancing waves, the second of which is due to reflection of the first at a free end. According to p. 220 the displacement of the original wave at time t and at a distance x along a string or rod of length l is

$$y_x = r \sin \left[2\pi \left(\frac{t}{T} - \frac{x}{\lambda} \right) \right].$$

The distance of this point from the reflecting end is $l - x$. Since there is no phase change on reflection, the motion of the point x due to the reflected wave is the same as that which a point at a distance $2(l - x)$ farther along the string would have if the reflecting end were not present and the string were of unlimited length. The distance of this imaginary point from the original end of the string is $x + 2(l - x) = 2l - x$. Its displacement would therefore be

$$y_x' = r \sin \left[2\pi \left(\frac{t}{T} - \frac{2l - x}{\lambda} \right) \right].$$

Hence at the point x the superposition of the incident and reflected waves gives the resultant displacement

$$Y_x = y_x + y_x' = r \left\{ \sin \left[2\pi \left(\frac{t}{T} - \frac{x}{\lambda} \right) \right] + \sin \left[2\pi \left(\frac{t}{T} - \frac{2l - x}{\lambda} \right) \right] \right\}.$$

Making use of the relation

$$\sin \alpha + \sin \beta = 2 \sin \frac{\alpha + \beta}{2} \cos \frac{\alpha - \beta}{2},$$

the expression for Y_x can be transformed to

$$Y_x = 2r \sin \left[2\pi \left(\frac{t}{T} - \frac{l}{\lambda} \right) \right] \cos \left[2\pi \left(\frac{l - x}{\lambda} \right) \right].$$

This is the equation of the stationary wave.

The value of the factor $\cos [2\pi(l - x)/\lambda]$ depends only upon the position of the point considered. When it is equal to zero, Y_x also remains equal to zero. The condition for this is

$$2\pi \left(\frac{l - x}{\lambda} \right) = (2n + 1) \frac{\pi}{2},$$

or

$$x = l - \frac{\lambda(2n + 1)}{4},$$

where n can have any integral value including 0. Thus we obtain the positions of the **nodes**: for $n = 0$, $x = l - \frac{1}{4}\lambda$; for $n = 1$, $x = l - \frac{3}{4}\lambda$, &c.

When $x = l$ the cosine factor in the expression for Y_x becomes equal to 1. Hence at the free end ($x = l$) of the string we have the maximum amplitude $2r$; this end is an **antinode**. The nodes lie at equal distances $\frac{1}{2}\lambda$ apart. The first one is at a distance $\frac{1}{4}\lambda$ from the free end.

Reflection at a Fixed End.—In this case there is a reversal of phase on reflection. We can take this into account by adding half a wave-length to the

distance $2l - x$ used in the preceding investigation of reflection at a free end. For the unreflected wave we have the same displacement at the point x as before, viz.:

$$y_x = r \sin \left[2\pi \left(\frac{t}{T} - \frac{x}{\lambda} \right) \right].$$

But for the reflected wave we now have

$$y_{x'} = r \sin \left[2\pi \left(\frac{t}{T} - \frac{2l - x + \lambda/2}{\lambda} \right) \right].$$

The resultant displacement due to the superposition of both waves is found by addition and becomes after transformation

$$Y_x = 2r \sin \left[2\pi \left(\frac{t}{T} - \frac{l + \lambda/4}{\lambda} \right) \right] \cos \left[2\pi \left(\frac{l - x + \lambda/4}{\lambda} \right) \right].$$

This is the equation of the stationary wave.

The value of the cosine factor again depends only upon the variable x , i.e. upon the position of the point. The condition that this factor shall vanish is

$$2\pi \left(\frac{l - x + \lambda/4}{\lambda} \right) = (2n + 1) \frac{\pi}{2}$$

or

$$x = l - \frac{n\lambda}{2},$$

where n may have any integral value including 0. For $n = 0$, $x = l$; $n = 1$, $x = l - \frac{1}{2}\lambda$; $n = 2$, $x = l - \lambda$; $n = 3$, $x = l - \frac{3}{2}\lambda$; &c. Thus the nodes are situated at distances $\frac{1}{2}\lambda$ apart and the fixed end of the string, for which $x = l$, is a node.

Amplitude of Stationary Waves.—In the case of reflection at a fixed end the positions of the antinodes are given by

$$x = l - \frac{n\lambda}{2} - \frac{\lambda}{4}.$$

Substituting this in the equation for Y_x , the cosine factor assumes the value ± 1 . The expression for the displacement is then

$$\begin{aligned} Y_x &= \pm 2r \sin \left[2\pi \left(\frac{t}{T} - \frac{l + \lambda/4}{\lambda} \right) \right] = \pm 2r \sin \left[2\pi \left(\frac{t}{T} - \frac{l}{\lambda} \right) - \frac{\pi}{2} \right] \\ &= \mp 2r \cos 2\pi \left(\frac{t}{T} - \frac{l}{\lambda} \right). \end{aligned}$$

The same result is obtained for the antinodes in the case of reflection at a free end. Hence:

The amplitude at the antinode of a stationary wave is twice that of each of the component advancing waves.

Demonstration of Wave Motion with Mach's* Wave Apparatus.—This (fig. 23) consists of a row of pendulums of equal length at equal distances apart. Each is suspended upon two strings, so that it can only swing in the direction at right angles to the plane of the strings. When this direction is at right angles to the row, the apparatus can be used to demonstrate a transverse wave. The pendulums are set swinging in succession, each one a certain constant time after the preceding one; this is done by displacing all the pendulums to the same extent by means of a long bar and then withdrawing the bar with uniform velocity

* ERNST MACH (1838–1916), Professor of Physics in Prague from 1867 to 1895, then Professor of Philosophy at Vienna until 1901.

in the direction of the row. In this way each pendulum is released the same length of time after the preceding one and a representation of a transverse wave of the kind already described is produced.

By means of a special device it is possible to turn the suspensions of all the pendulums simultaneously through any desired angle, e.g. 90° . In this way the previously transverse swings become swings in the direction of the row and a representation of a longitudinal wave is produced. This is the mechanical realization of fig. 21, p. 235.

Alternatively, the block *s* may be moved with uniform velocity along the rail *e* beneath the pendulums, so as successively to displace each of them by the same small amount and release it again. The motion of each pendulum thus begins the same length of time later than the preceding one, and the representation of a longitudinal wave is produced directly.

As already mentioned, it is possible by rotation of the suspensions to turn the planes of oscillation of the pendulums from the transverse to the longitudinal direction and vice versa. This shows clearly that both kinds of waves are governed

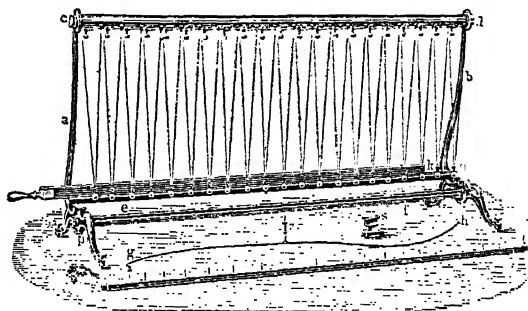


Fig 23.—Mach's Wave Apparatus

by the same law and that the only difference between them lies in the direction of oscillation of the particles relative to the direction of propagation of the wave.

For the demonstration of stationary transverse waves use may be made of the curved wire *gh*, which can be turned about an axis *z* through its middle point. For stationary longitudinal waves the bar *st* is used.

The individual pendulums of Mach's wave apparatus move independently of one another, since there is no coupling between them. Their motion is therefore only a *representation* of a wave. In order to reproduce wave motion exactly, the individual pendulums must be coupled together, say by elastic strings, in some such way as in the net shown in fig. 16, p. 222, or the Julius wave apparatus shown in figs. 24 and 25, p. 204.

5. General Laws of Wave Propagation

In § 1, p. 208 *et seq.*, the spreading of a plane wave system has already been considered in the special case of water waves. We will now give a more general derivation of the observed laws.

1. **Wave Front.**—In the figures of § 1, p. 208 *et seq.* certain lines can be seen, whose points all have the same phase. Thus, for example, the wave centre in fig. 5, p. 213, is surrounded by circles corresponding to equality of phase, say crests. The observation of the formation of such a wave system shows how the waves spread out in circles across

the surface of the water. The locus of all the points which the wave motion has reached at a given moment is called the wave front. In the case of waves on the surface of water the wave front is a *line*.

If the wave system is not two-dimensional but three-dimensional, as, for instance, in the case of sound waves considered below (p. 251), the locus of the points reached by the wave motion at any given instant is not a line but a *surface*. In an *isotropic* medium, i.e. a medium in which the velocity of propagation is the same in all directions, the wave front is a *spherical surface*.

Since the energy must be the same for every wave front, and the area of a sphere is proportional to the square of the radius of the sphere, the energy of the wave per unit area of front must be inversely proportional to the square of this radius.

In the case of a wave spreading in three dimensions in an isotropic medium the energy of the vibrating particles varies inversely as the square of the distance from the wave centre.

In anisotropic media the wave front is not spherical. In certain cases (of importance in optics) it may be the surface of an ellipsoid.

Under certain circumstances (e.g. at very great distances from the wave centre and when only a very small part of the front is considered) the wave

front may be a *plane*. In this case we speak of *plane waves*.*

2. The Huygens-Fresnel Principle.—The principle of the *superposition* or *interference* of waves (§ 1, p. 211 *et seq.*) is of great importance for the question of wave propagation. The reason for this lies in Huygens' principle, which has already been enunciated on p. 216:

Every point of a wave front may be regarded as the centre of a new elementary wave system. The resultant system produced by the interference of all these elements is identical with the actual single wave.

Huygens' expression of the principle named after him was as follows. If M (fig. 24) is the centre of a wave system and if the wave has spread to the spherical front K_1 , every point of this spherical surface can be regarded as the centre of spherically spreading elementary waves. The front of the resultant wave formed by the superposition of all these elements is then the spherical *envelope* K_2 . This is identical with the surface of the sphere with the same centre M as

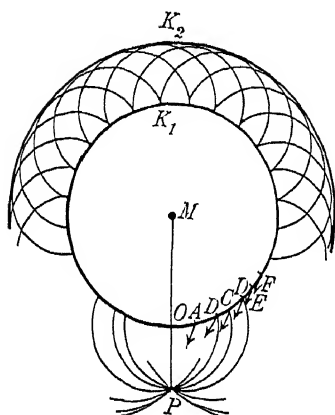


Fig. 24.—Huygens' Principle: the Spherical Wave as the Envelope of the Elementary Waves.

* These belong therefore to a *three-dimensional* wave system.

the original wave and a radius equal to the sum of the radii of the sphere K_1 and an elementary sphere.

If we wish to find the state of motion at any point P (see fig. 24) of the wave system, we must consider the superposition of all the elementary waves at this point.*

The complete solution of this problem is rather complicated, and can only be obtained with the help of the integral calculus. We will therefore simplify the problem by considering plane wave fronts (cf. fig. 8, p. 215), i.e. we will imagine the centre M of the wave to be at such a great distance that the arc of the circle K_1 (fig. 24) may be regarded as a straight line.

With this simplification we can consider the plane wave front MM' (fig. 25) to move in a direction at right angles to itself. Let it have arrived at the position NN'. Then by Huygens' principle each point O of NN' is the centre of an elementary spherical wave and PP' is the common tangent plane to all of these elements.

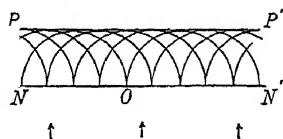


Fig. 25.—Huygens' Principle:
Plane Wave Front

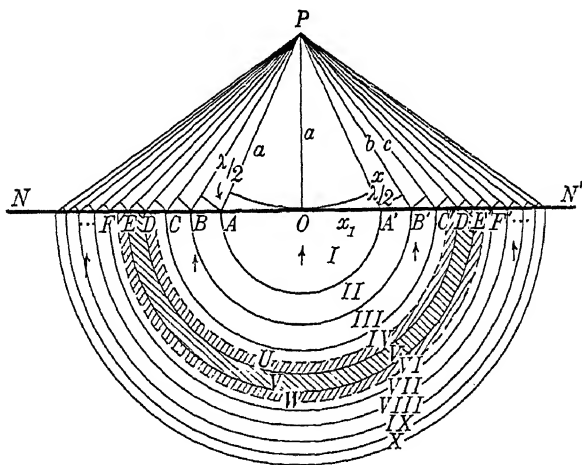


Fig. 26.—Fresnel's Zones

We will investigate the state of motion at a point P (fig. 26) at a distance a in front of NN'. For this purpose drop the perpendicular PO from P on to NN'.

* This method was originated by FRESNEL with the help of the interference principle put forward by THOMAS YOUNG. A. J. FRESNEL (born 1788 at Broglie, died 1827 at Ville-d'Avray near Paris), originally an engineer; his work, begun in 1814, helped greatly to bring about the acceptance of the undulatory theory of light. His "Mémoire sur la diffraction de la lumière", for which he received a special prize from the Academy, definitely established the theory. He treated most optical processes by means of the theory of the elastic vibration of the *luminiferous ether*. He is also famous as the inventor (1823) of "zone lenses", i.e. large lenses consisting of a combination of a large number of individual prisms, by means of which the light from lighthouses is concentrated, partly by refraction and partly by total reflection, so that it can be seen at very great distances.

The point O is called the pole of the point P. Also draw the straight lines PA, PB, PC, . . . , &c., and PA', PB', PC', . . . , &c., such that

$$PO = a, PA = PA' = a + \frac{1}{2}\lambda, PB = PB' = a + 2 \cdot \frac{1}{2}\lambda, PC = PC' = a + 3 \cdot \frac{1}{2}\lambda, \dots \&c.,$$

i.e. so that each of the points A, B, C, . . . , &c., is half a wave-length farther from P than the preceding one. This construction must be carried out for the whole of the plane wave front. The system of lines from P to the plane then form a system of conical surfaces intersecting the plane in a system of concentric circles. These circles are shown in the lower half of fig. 26. In order to obtain the correct three-dimensional figure, this lower half must be imagined to be turned about NN' as axis until it stands at right angles to the plane of the paper. Thus the upper and lower halves of fig. 26 represent the side elevation and plan respectively of the whole three-dimensional system. The diameter AO = x_1 of the first circle can be calculated from the right-angled triangle POA. We have

$$x_1^2 = (a + \frac{1}{2}\lambda)^2 - a^2 = a^2 + a\lambda + \frac{\lambda^2}{4} - a^2 = a\lambda + \frac{\lambda^2}{4}.$$

Now we suppose that λ is so small in comparison with a that the quadratic term $\lambda^2/4$ can be neglected in comparison with the term $a\lambda$ of the first degree. We can then put $x_1 = \sqrt{a\lambda}$.

In the same way the radius x_n of the n th circle can be obtained from the equation

$$x_n^2 = \left(a + \frac{n\lambda}{2}\right)^2 - a^2.$$

Assuming that $n\lambda$ is small in comparison with a we have from this

$$x_n = \sqrt{na\lambda}.$$

The different circles have the areas

$$S_1 = \pi x_1^2 = \pi a\lambda, S_2 = \pi x_2^2 = 2\pi a\lambda, \dots, S_n = \pi x_n^2 = n\pi a\lambda.$$

The ring-shaped regions between the successive circles are all of the same area, namely, that of the innermost circle $S_1 = \pi a\lambda$.

Each of these ring-shaped regions is called a **Fresnel zone**. Hence all the Fresnel zones contain the same number of equal elements of area, i.e. from each Fresnel zone originate the same number of elementary waves.*

Now each successive circle is half a wave-length farther from P than the one before it. Hence if elementary waves set out from every point of the plane wave front NN' with the same phase, they will not arrive at P in the same phase; for to every point of a zone, e.g. of the n th zone, there corresponds a point of the next zone, the $(n+1)$ th, from which waves arrive at P in exactly opposite phase. If the amplitudes of these elementary waves were equal, those from the first zone would be neutralized at P by those from the second. Similarly the elementary waves from the third and fourth zones, as well as from each successive pair of zones, would neutralize each other at P, which would therefore remain always at rest.

Actually, however, the amplitude of the elementary waves decreases as they spread out from their centres. Without going into details with regard to the law

* If the wave front from which the elementary waves originate is not a plane but a spherical surface, the FRESNEL zones are again equal, provided that $\frac{1}{2}n\lambda$ can be neglected in comparison with a .

of this decrease, it can be shown * that the amplitude of any elementary wave is equal to the arithmetical mean of the amplitudes of those on either side of it. Hence the effect of all the elementary waves from any given Fresnel zone is neutralized by the effect of the contiguous halves of the two neighbouring zones. In fig. 26 the fifth zone V and the contiguous halves of the fourth zone U and the sixth zone W are shown shaded. The total effect of all these shaded parts at the point P is zero.

If the effect of any zone is z_n , where n is the ordinal number of the zone, the total effect of all the zones of the unlimited plane wave from NN' is

$$z = z_1 - z_2 + z_3 - z_4 + z_5 - z_6 + \dots$$

This can be transformed to

$$z = \frac{1}{2}z_1 + (\frac{1}{2}z_1 - z_2 + \frac{1}{2}z_3) + (\frac{1}{2}z_3 - z_4 + \frac{1}{2}z_5) + \dots$$

In this each of the expressions in brackets vanishes and the total effect simplifies to

$$z = \frac{1}{2}z_1,$$

since in the case of an unlimited plane wave front the subsequent terms of the series for z decrease continually and tend to the limit zero.

Hence it follows that:

All the elementary waves sent out according to Huygens' principle from all the points of an infinite plane (or spherical) wave front have the same total effect at a point as the half of the first elementary zone surrounding the pole of the point.

From this follows at once the validity of Huygens' principle in its original form for infinite plane waves. The derivation of this principle for infinite waves of other shapes follows the lines of the above example. The strict proof cannot, however, be given here.

* The difference of amplitude due to the small difference in distance between successive zones is also extremely small. If we consider the amplitude of the waves arriving at P from the elementary zones as a function of the number n of the zone, i.e. if we write

$$z_n = f\left(a + \frac{n\lambda}{2}\right),$$

we can regard the increase $\frac{1}{2}\lambda$ of $(a + \frac{1}{2}n\lambda)$ corresponding to the passage from one zone to the next as the differential of $(a + \frac{1}{2}n\lambda)$. According to the rules of the differential calculus we may then write approximately

$$z_{n+1} = f\left[a + (n+1)\frac{\lambda}{2}\right] = f\left(a + \frac{n\lambda}{2}\right) + \frac{\lambda}{2}f'\left(a + \frac{n\lambda}{2}\right) = z_n + \frac{\lambda}{2}f'\left(a + \frac{n\lambda}{2}\right),$$

$$z_{n+2} = f\left[a + (n+2)\frac{\lambda}{2}\right] = f\left(a + \frac{n\lambda}{2}\right) + 2 \cdot \frac{\lambda}{2}f'\left(a + \frac{n\lambda}{2}\right) = z_n + 2 \cdot \frac{\lambda}{2}f'\left(a + \frac{n\lambda}{2}\right).$$

Small terms of higher order have been neglected. From this we obtain

$$z_n + z_{n+2} = 2z_{n+1} \quad \text{or} \quad z_{n+1} = \frac{z_n + z_{n+2}}{2}.$$

3. Diffraction.—The condition that a wave shall have the same effect at a point as that of the half of the central Fresnel zone is that the wave is of infinite extent; for only then do the effects of the other zones neutralize each other and only then can the effects of the farthest zones be set equal to zero. If on the contrary we are dealing with a limited portion of an advancing wave, the behaviour is essentially different.

As a practical application of Huygens' principle we will consider more closely the case (already represented for water waves in fig. 9, p. 215) of a screen with an opening in it. We will investigate the effect behind the screen of a system of plane waves incident upon it.

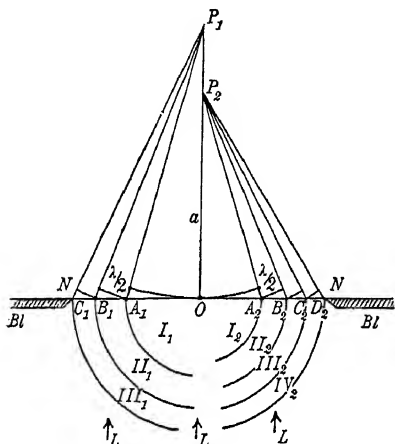


Fig. 27.—Diffraction due to a Small Circular Hole

In fig. 27 Bl represents the central portion of a screen with the circular opening NN . A system of plane waves is incident upon it in the direction L (in the figure from below upwards). Let O be the middle point of the opening and P_1 and P_2 any two points upon the perpendicular to the screen through O . About P_1 (and similarly about P_2) we describe concentric spherical surfaces, the innermost of which has the radius a and passes through O . The radius of each successive sphere is greater by $\frac{1}{2}\lambda$ than that of the preceding one, i.e.

$$P_1O = a, \quad P_1A_1 = a + \frac{1}{2}\lambda, \quad P_1B_1 = a + 2 \cdot \frac{1}{2}\lambda, \dots, \&c.$$

These spheres intersect the opening and divide it up into Fresnel zones. In fig. 27 it has been assumed that the spherical surfaces about P_1 as centre give rise to three zones and those about P_2 as centre to four zones.

Now in every case a is to be considered as very much larger than $\frac{1}{2}\lambda$, so that the amplitudes of the elementary waves from the points A_1, B_1, C_1 , &c., of the small opening NN are practically equal when they arrive at the point P_1 (or P_2).

The elementary zones I, II, III, &c., are of the same area (see above), and the phases of waves from any two consecutive zones are opposite; therefore the effect of each pair of consecutive zones is zero. From this it follows that all points P_1 , which are at such a distance from the middle O of the opening that the corresponding number of Huygens' zones in the opening is odd, must oscillate with great amplitude. Similarly, all points P_2 , for which the corresponding number of elementary zones is even, must remain at rest.

In the same way it can also be shown that there are points lying off the axis OP which are at rest or oscillating with maximum amplitude according to their distance from the centre of the opening. In the case of a circular opening and of spherical elementary waves the loci of all such points are circles in planes parallel to the plane of the opening. Hence:

When a system of plane waves is incident upon a screen with a circular hole in it, the whole of the space behind the screen is filled with waves in

such a way that in planes parallel to the plane of the opening there exist ring-shaped regions of maximum or zero amplitude.

The appearance of these interference effects is an extremely important criterion for the presence of a wave motion. It was with the help of experiments of this kind that YOUNG and FRESNEL succeeded in proving the undulatory nature of light.

Fig. 28 (after ARKADIEV) shows reproductions of photographs obtained with light beams which have passed through small openings. In the first picture the opening was of such a size as to include seven Fresnel zones; in the second picture, eight. Hence in the first case the middle of the diffraction pattern is bright, in the second dark. Further examples of this kind will be treated in Vol. IV (Optics).

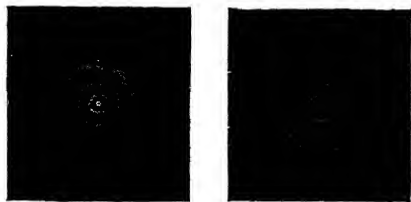


Fig. 28.—Patterns formed by Diffraction at Small Holes

An especially important case is that in which the waves are incident upon a large number of regularly arranged openings (a so-called *grating*). When the nature of the arrangement is known, measurement of the positions of the maxima and minima of intensity behind the screen provide a particularly suitable method of determining the wave-length λ of the waves. This very important method is also described more fully in Vol. IV.

4. Reflection.—At the boundary surface between two media in which the velocity of propagation of the wave motion is different, a more or less complete reflection occurs. We will consider on the basis of Huygens' principle a few special cases similar to those represented for water waves in figs. 10, 12, 13 and 14 (pp. 216–218).

Reflection of Plane Waves at a Plane Boundary (Mirror) (cf. figs. 10 and 11, pp. 216 and 217). In fig. 29 let ZZ be the plane surface separating two media. The plane waves with the front A_1A_2 are incident in the direction of the arrow E . If the incidence is slanting, the point of the wave front corresponding to A_1 reaches the surface ZZ first at the point C_1 and gives rise here to a system of elementary waves which spread spherically. At this moment the point of the wave front corresponding to A_2 has reached C_2 . By the time this point of the front has reached the plane ZZ at the point D_2 , the spherical elementary wave from C_1 has already covered a distance equal to C_2D_2 . Thus the radius of the wave front of this elementary wave is $C_1D_1 = C_2D_2$. Any other part of the wave (such as that dotted in the figure) has by this time covered after reflection a distance shorter than C_2D_2 . The spherical front of the corresponding elementary wave is represented by the dotted circle in the figure. Thus when the plane wave is incident upon the plane surface ZZ , the points of the surface struck by the wave become centres of elementary waves, which combine to give the new front D_1D_2 . The direction of propagation of the reflected wave is at right angles to the front D_1D_2 , i.e. that of the arrow R . The reflected wave front subsequently reaches the position F_1F_2 .

Draw the perpendiculars C_1L_1 and D_2L_2 to ZZ at the points C_1 and D_2 re-

spectively. The angle of incidence is $A_1C_1L_1 = \alpha$ and the angle of reflection $L_2D_2F_2 = \beta$.

Since $C_1D_1 = C_2D_2$, therefore $\triangle C_1D_2C_2$ is congruent with $\triangle C_1D_2D_1$, whence it follows that $\angle C_2C_1D_2 = \angle D_1D_2C_1$. Now $\angle C_2C_1D_2 = \alpha$ and $\angle D_1D_2C_1 = \beta$. Therefore $\alpha = \beta$. This equation expresses the law of reflection:

The angle of incidence is equal to the angle of reflection.

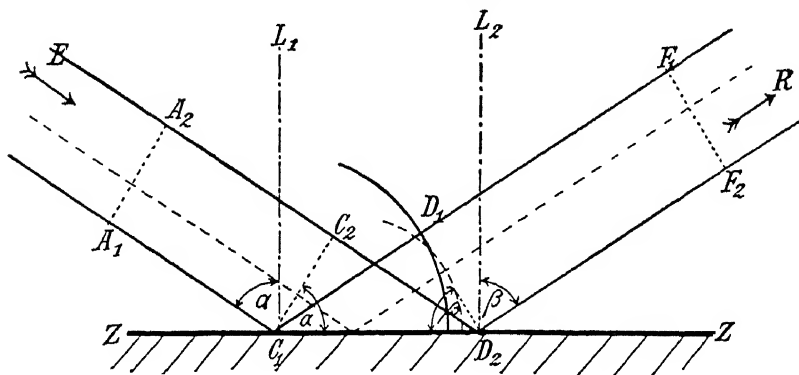


Fig. 29.—Reflection of Plane Waves at a Plane Surface

Reflection of Plane Waves at a Spherical Surface (Concave Mirror).—Consider a plane wave with the wave front W (fig. 30) to be incident in a direction parallel to the axis AC upon a spherical reflector represented by the shaded circular arc. At the moment when the wave front has reached D , the point upon the axis has only reached L . The front is then represented by the dotted line LD . The point D now becomes the centre of new elementary waves which, by the time the point L has reached the reflector at C , have covered a distance equal

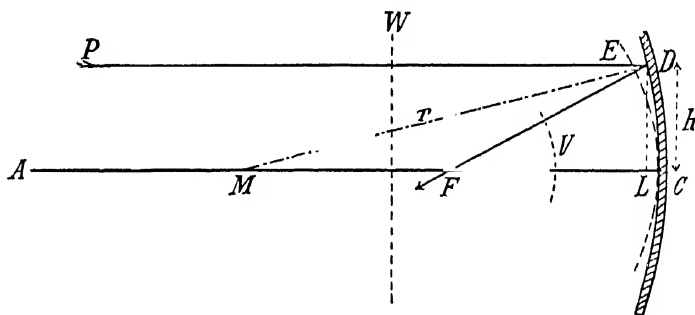


Fig. 30.—Reflection of Plane Waves at a Concave Reflector

to LC . The same consideration applies for all the points of the incident wave front incident upon the reflector between D and C . The reflected wave front CE is then the envelope of all the elementary waves. If we confine our attention to parts of the wave lying near the axis, CE can be regarded as a circular arc. The reflected wave is therefore spherical. At a later time the reflected wave front has the position V and eventually shrinks to a point at F . Here all the energy of the reflected wave is concentrated. In the special case when the incident wave is plane and parallel to the axis this point is called the *focus* (cf. fig. 12, p. 217).

Let r be the radius of the reflector and M its centre of curvature, and $f = FE = FC$ the radius of the reflected wave front. Let $LD = h$. Since we

are only considering that portion of the wave in the neighbourhood of the axis, we may regard arc as equal to chord, and therefore $h = LD = CD = CE$. Then by geometry

$$\text{LC} : h = h : 2r \text{ and } (\text{ED} \div \text{LC}) : h = h : 2f.$$

Hence, since $ED = LC$, we have

$$2r = \frac{h^2}{LC} \quad \text{and} \quad 2f = \frac{h^2}{2LC},$$

and therefore

$$\mathbf{f} = \frac{1}{2}\mathbf{r}.$$

That is to say, in the case of a spherical reflector the focus lies midway between the centre of curvature and the reflector itself.

Reflection of Spherical Waves at a Spherical Surface.—In fig. 31 G is the centre of the incident wave system and is such that GC is greater than the radius MC of the reflector. The surface W represents a position of the incident wave front.

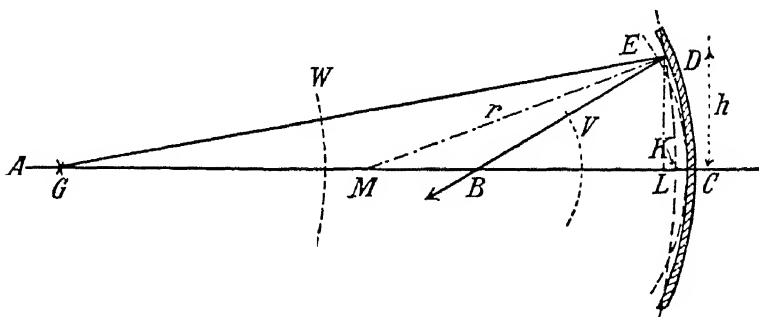


Fig. 31.—Reflection of a Divergent Wave System at a Concave Reflector

At the moment when a point of this front has reached the reflector at D, the point on the axis is still in front of the reflector at K. At the moment when this axial point has reached the reflector at C, the points lying off the axis have already been reflected and have given rise to a system of elementary spherical waves with a wave front CE. This front is itself spherical. At a later time it arrives at the position V and eventually shrinks to the point B.

This point B is called the image of the point source G. If $-u = GD = GK$ is the distance of the source from the reflector (negative, because the direction of the incident wave is opposite to that of the reflected wave), $v = BD = BC$ the distance of the image from the reflector and $r = MD$ the radius of curvature of the reflector, then, since CD can be put equal to h , we have as above

$$(\text{ED} + \text{LK} + \text{KC}) : h = h : 2v,$$

$$\text{LK} : h = h : -2u$$

and

$$\text{LK} \vdash \text{KC} : h = h : 2r.$$

Since $ED = KC$, therefore

$$2KC + LK = \frac{h^2}{2\eta},$$

$$\text{LK} = -\frac{\hbar^2}{2u},$$

$$\text{LK} + \text{KC} = \frac{h^2}{2r}.$$

Adding the first two equations we obtain

$$2(LK + KC) = -\frac{h^2}{2u} + \frac{h^2}{2v}.$$

Combining this with the third equation we have

$$\frac{h^2}{2v} - \frac{h^2}{2u} = \frac{2h^2}{2r}.$$

Therefore

$$\frac{1}{v} = \frac{1}{u} + \frac{2}{r} = \frac{1}{u} + \frac{1}{f}.$$

This is the equation connecting the distance of the source, the distance of the image, and the radius of curvature of the reflector (concave mirror).

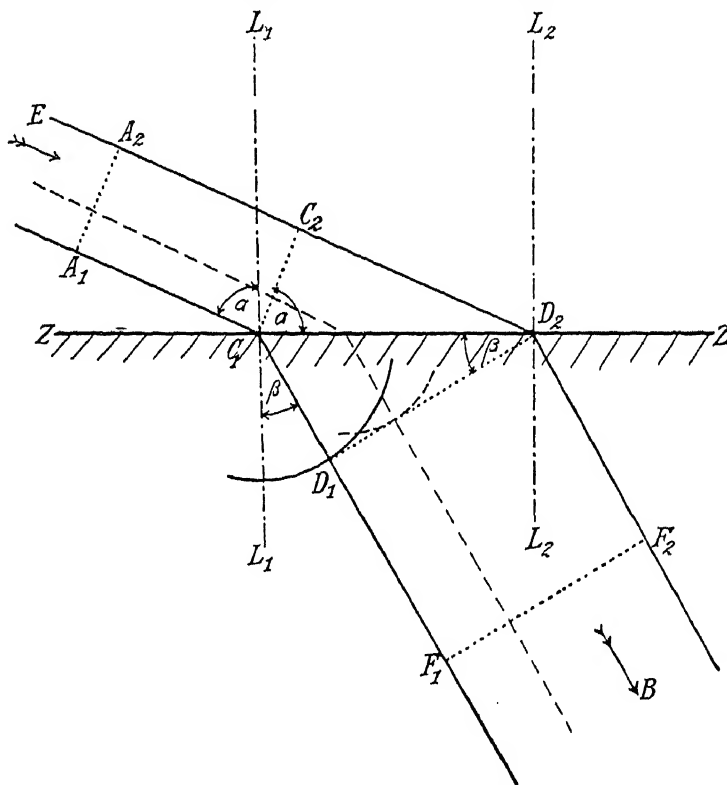


Fig. 32.—Wave Theory of Refraction

The derivation of the corresponding equation for convex mirrors is analogous to the above. It is seen from fig. 14, p. 218, that in this case the new system of waves formed by reflection has its centre behind the reflector.

5. Refraction.—When a wave is incident upon the boundary surface between two media in which the velocity of propagation of the waves is different, the reflection (see above) is only partial. A part of the wave passes through into the second medium, but with a sudden change of direction. This phenomenon is called *refraction*.

We will consider the case of plane waves incident upon a plane boundary surface between two media (fig. 32). Let the direction of incidence be that of the arrow E. At the moment when the extreme lateral point of the wave front corresponding to A_1 has reached the surface at C_1 , the other extreme point corresponding to A_2 has only reached C_2 . The point C_1 becomes the centre of a new elementary wave, which spreads into the second medium below ZZ. Let the velocity v_2 of propagation in the second medium be smaller than that v_1 in the first. By the time the extreme point corresponding to A_2 has reached ZZ at D_2 , the spherical front of the elementary wave sent out from C_1 will have reached the position represented by the circle through D_1 . If the ratio of v_2 to v_1 is 1 to n , then

$$C_1D_1 = \frac{1}{n} C_2D_2.$$

An intermediate point of the incident wave front (see the dotted line parallel to A_1C_1 and A_2C_2) gives rise to an elementary spherical wave whose front will have reached the corresponding position represented by the dotted circle. Thus the total refracted wave front in the second medium is the common tangent D_1D_2 to all the elementary waves. The refracted wave moves in a direction at right angles to this front, i.e. in the direction of the arrow B. At some time after refraction the wave front reaches the position F_1F_2 .

At C_1 and D_2 draw the perpendiculars L_1L_1 and L_2L_2 respectively to the surface ZZ. The angle of incidence is $\angle A_1C_1L_1 = \alpha$. The angle of refraction is $\angle D_1C_1L_1 = \beta$. From the figure it is seen also that $\angle C_2C_1D_2 = \alpha$ and $\angle C_1D_2D_1 = \beta$. In $\triangle C_1C_2D_2$ we have $\sin \alpha = C_2D_2/C_1D_2$. In $\triangle C_1D_1D_2$, $\sin \beta = C_1D_1/C_1D_2$. By division, $\sin \alpha/\sin \beta = C_2D_2/C_1D_1$. But from the ratio of the velocities of propagation in the two media we have $C_2D_2/C_1D_1 = n$.

Therefore
$$\frac{\sin \alpha}{\sin \beta} = n = \frac{v_1}{v_2}.$$

The ratio of the sine of the angle of incidence to the sine of the angle of refraction is equal to the ratio of the velocities of propagation of the waves in the respective media.

This ratio n is called the **refractive index**.

SOUND

CHAPTER I

Sources of Sound

1. Scope of the Subject

1. Acoustics or the science of sound is a special branch of the science of vibrations. It includes the theory of elastic longitudinal waves in gases and of the vibrations of the bodies producing them. As a rule only such vibrations are considered as produce the sensation of sound in the ear; recently, however, it has become usual also to include in acoustics vibrations of frequencies far above the upper limit of audibility (see below) (ultra-sonic waves).

If a bell be placed under the receiver of an air pump and the air removed, the bell is still set vibrating by the strokes of the hammer, but in spite of this it cannot be heard. From this it follows that the propagation of sound is normally through the air. Care must be taken in the above experiment, however, that the vibrations of the bell are not transmitted by means of solid bodies to the external walls of the receiver. Thus the bell must be placed upon some soft substance or suspended by an elastic thread (e.g. of wool or rubber).

2. **Limits of Audibility.**—In order that it may be heard, the vibration must have a certain strength and a certain frequency. The strength or intensity of the waves (elastic pressure waves in the air) can be measured by means of the pressure variation (**pressure amplitude**). The unit of frequency is the hertz (1 cycle per second). The minimum intensity which a sound wave must have in order to be audible is called the **threshold intensity of audibility**. If the energy increases above a certain value (**the threshold intensity of feeling**) a sensation of pain is produced in the ear. Further, the vibration must have a frequency above a certain minimum (**lower pitch limit of audibility**) in order to be perceived as sound. This limit lies at about 16 hertz. Frequencies above 20,000 hertz are likewise inaudible (**upper pitch**

limit). Fig. 1 gives graphs of these relationships. The pressure amplitudes in dynes per cm.² are plotted as ordinates and the frequencies in hertz as abscissæ. The region of audibility lies between the two curves, which represent the thresholds of audibility and feeling. (See further § 3, p. 282 *et seq.*)

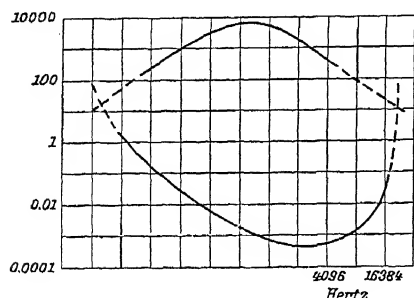


Fig. 1.—Range of Audibility. (Ordinates represent pressure amplitudes in dynes/cm.²; upper curve, threshold of feeling; lower curve, threshold of audibility.)

sounds. These usually involve rather complicated vibrations. A sound due to a pure sine vibration will be called a *note*.* According to Fourier's theorem (p. 223) any periodic vibration can be analysed into a sum of sine vibrations; hence every musical sound can be regarded as a combination of notes.

A note is characterized by its *pitch* and its *intensity* or *loudness*.

2. Pitch

1. What Property of the Vibration is perceived as Pitch?

Experiment.—For the investigation of pitch we will consider first the processes involved in the vibration of a string. We stretch the string as in fig. 2. The apparatus depicted is called a *monochord*. According to p. 228 the frequency of vibration is

$$v = \frac{1}{2l} \sqrt{\frac{p}{d}}.$$

Any desired length of the string can be divided off by means of movable bridge-pieces placed beneath it. In this way, therefore, the frequency of vibration of the section under investigation can be varied at will. This frequency can be calculated from the length, mass per unit length (obtainable from the weight of a known length), and the tension of the string (measured by the weight in the scale pan—see figure).

* The sound due to a pure sine vibration (i.e. a simple harmonic vibration) is more strictly called a *simple tone*, or *pure tone*. But both words, tone and note, are used in various senses in musical and ordinary language. We speak, for example, of the tone of a piano, of an interval of a tone or semitone, of the note of the nightingale, of the notes of the musical staff. In less exact usage the terms note and musical sound are sometimes taken to be equivalent. This gives rise to a difficulty in deciding upon the frequency, to avoid which the lowest frequency is taken as the frequency of the musical sound, although often it is only weakly represented.

The shorter the length of the string or the greater its tension, i.e. the greater ν , the higher becomes the pitch of the note.

The characteristic property associated with pitch is frequency. A higher pitch always corresponds to a higher frequency.

If we produce the same frequency in two different ways, firstly, by choosing the right length of the string with a given load, and secondly, by choosing the right load with a given length, we get the same pitch in both cases. Thus pitch depends only upon frequency.

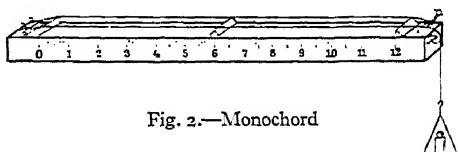


Fig. 2.—Monochord

Further Experiment.—A circular disc with a ring of holes through it at equal distances parallel to its periphery (siren, fig. 42, p. 274) is made to rotate rapidly and uniformly. A stream of air blown against the holes is thus periodically interrupted and a note is heard. The frequency can be calculated from the number of holes and the speed of revolution of the disc. A toothed wheel can also be used, a piece of card being held against its teeth. The pitch becomes higher as the speed of revolution is increased. Here again notes of equal frequency (compared with those of the monochord) have the same pitch as heard by the

2. Designation and Graphical Representation of Notes.—In the comparison of notes of different pitch it is found that certain pairs of notes appear very similar. These are notes whose frequencies are in the ratio 1 : 2. The higher is called the **octave** of the lower. For the purposes of music certain notes have been selected from the infinite number of possibilities and have been designated by letters. For historic reasons it is usual in the simplest case to have six notes between the two notes of the octave, the lower of which is called *do* and the upper *do*¹. The six intermediate notes have frequencies in the simplest possible ratios to that of the *do*. (See table below.)

The ratio of the frequencies of two notes is called the **interval** between them.

The notes are designated from *do* upwards by the letters C, D, E, F, G, A, B. Thus we have the following simplest scale:

Name	do	re	mi	fa	sol	la	si	do ¹
Relative frequency	1	9/8	5/4	4/3	3/2	5/3	15/8	2
Interval of Successive Notes	9/8	10/9	16/15	9/8	10/9	9/8	16/15	
Designation	C	D	E	F	G	A	B	c
Smallest integers proportional to frequencies	24	27	30	32	36	40	45	48

The octave do^1 is designated by the same letter as do , but in order to distinguish between them the higher is designated by a small letter and the lower by a large letter. Still higher octaves are designated by c^1 , c^{11} , &c., lower ones by C_1 , C_{11} , &c.

The interval between consecutive notes may have three values, namely, $8:9 = C:D = F:G = A:B$; or $9:10 = D:E = G:A$; or $15:16 = E:F = B:c$. The difference between the intervals $9/8$ and $10/9$ (namely, $9/8 \div 10/9 = 81/80$) is small and only recognizable with difficulty. It is called a *comma*. The intervals $9/8$ and $10/9$ are called *major* and *minor tones* respectively. The interval $16/15$ is known as a *semi-tone* or *limma*.

It was decided by international agreement in 1885 to fix absolute pitch by taking as a^1 the note with the frequency 435 hertz (**French Pitch**).*

For graphical representation use is made of a *musical staff notation* in which the time is plotted roughly as abscissa

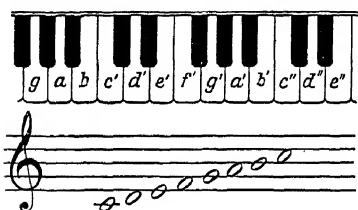


Fig. 3.—Piano Keyboard and Corresponding Staff Notation

and the logarithm of the frequency as ordinate. Fig. 3 shows an example of such a representation. In the case of the piano the notes actually used range from A_{11} to a^{1111} . The range used in the whole of music is from A_{11} to d^{1111} , i.e. from about 27 to 4700 hertz.

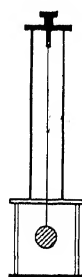


Fig. 4
Rayleigh
Disc

3. Loudness

1. **Measurement of Loudness or Intensity.**—The influence of loudness upon audibility has already been mentioned on p. 251. The intensity of sound is measured by the *quantity of energy* I *passing per second* through unit area at right angles to the direction of propagation. Its unit is therefore $\text{erg}/(\text{sec. cm.}^2) = 10^{-7} \text{ watt/cm.}^2$. The pressure amplitude p (unit: dyne/cm.^2) is also often used as a measure of intensity (see, for example, fig. 1, p. 252). The two are related by the equation

$$I = \frac{p^2}{2\rho_0 c},$$

where ρ_0 is the mean density of the air and c the velocity of sound.

In practical measurements the pressure amplitude may be determined directly by means of suitable manometers, or the intensity may be measured directly by converting the energy into electrical work which can be measured easily. The apparatus for these purposes cannot be discussed here.

* Concert pitch is 460 for a^1 . In physics it is convenient to put $a^1 = 426.66$ hertz, because then c^1 is 256, which is 2^8 .

2. Sound Pressure.—A third method makes use of the pressure effect of sound waves. When they are reflected at a wall, the sound waves exert a pressure upon it—the *sound pressure*. It is proportional to the **energy density** $\epsilon = I/c$, where I is the intensity and c the velocity of the sound. Further, bodies are attracted to the sound source when they are denser than the medium, and repelled from it when they are lighter than the medium in which the sound is propagated. (SCHELLBACH, 1870.) Thus, for example, a piece of paper is attracted by a sounding tuning fork. To measure the intensity use is made of the fact (LORD RAYLEIGH, 1882) that a very thin disc (of about 2 mm. diameter) tends, when hung up in the way of the sound, to set itself with its surface at right angles to the direction of propagation (fig. 4). The causes of this phenomenon are the same as those which give rise to the tendency of a falling sheet of paper to set itself at right angles to its direction of falling. The turning moment exerted upon the disc is proportional to the intensity of the sound. The *Rayleigh disc* is widely used for the measurement of sound intensity independently of frequency and wave form.

3. Variation of Intensity of Sound with Distance from the Source.

—Since sound consists of a system of waves, it spreads in the air in the same manner as the water waves shown on pp. 213–218, but with the differences that the advancing waves are longitudinal and that the spreading is in three dimensions, so that we have a system of spherical waves instead of circular waves. From this it follows that the intensity of spreading sound waves decreases more rapidly with the distance than that of water waves. Whereas in the plane system of water waves the mass of water set in motion is proportional to the distance from the centre of the wave system, the corresponding mass in the case of spherical sound waves is proportional to the square of the distance. From this it follows by theory that the intensity of sound, i.e. the energy imparted to a certain mass of air, ought to be inversely proportional to the square of the distance from the source (p. 240, see also below).

In the case of propagation of sound along tubes there is only a small decrease of intensity, because the energy of the vibrating masses of air cannot spread out in all directions (ear trumpet, speaking tube); the energy transmission takes place in a manner similar to that for a row of elastic balls (fig. 26, p. 205). For the same reason sounds are transmitted to greater distances along a stretched wire or thread (string telephone) than through the air. If a ticking watch be placed upon a table, then by placing the ear against the table the ticks can be heard at a greater distance than through the air. The reason for this is that in the table the energy transmission is only along a thin lamina and therefore with an intensity inversely proportional to the distance, whereas in the air the spreading is in three dimensions and

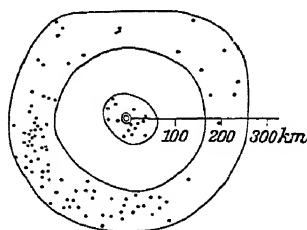


Fig. 5.—Zone of Silence in an Explosion (Moscow, 1920). (The dots show the places at which the explosion was heard.)

the intensity inversely proportional to the square of the distance.

It is remarkable that over very great distances the decrease of sound intensity is by no means of the above gradual and continuous character. Instead an intermediate zone of zero intensity (*zone of silence*, fig. 5) appears, while at greater distances the sound becomes audible again. For an explanation of this phenomenon see p. 277.

Sound waves of very high frequency, i.e. very small wave-length, are absorbed to a great extent in air. The distance over which the intensity falls to 1/100 of its original value is 40 cm. for a wave-length of 0.8 mm., but only 0.6 cm. for a wave-length of 0.1 mm. Hence above a frequency of 3,000,000 hertz no sound waves can be detected in air.

4. Quality or Timbre

Differences are often apparent between musical sounds of the same pitch and loudness. For instance, the sound of one and the same note, say a' , is different on the violin and on the clarinet. This difference is described by the term quality or timbre.

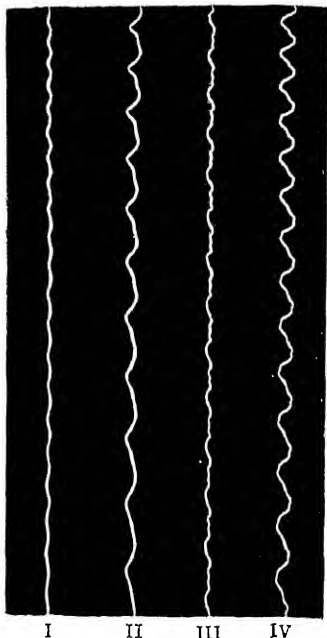


Fig. 6.—Vibration Forms of a Plucked String with Overtones

Even the same source can produce different qualities, if excited in different ways. Thus when a monochord is plucked first in the middle and then near one end, the note sounds “brighter” in the second case than in the first.

The investigation of sounding strings gives vibration figures like those shown in fig. 6. In I the string was plucked in the middle, in II about one-third of the way along, and in III and IV still nearer the end. It will be seen that the quality depends on the form of the vibration. The more complicated the form, the “brighter” the note sounds.

We have seen (p. 223) that complicated forms of vibration can be regarded as the superposition of different sine vibrations whose frequencies are multiples of the fundamental. These superimposed sine vibrations are called **overtones**, or **upper partials**. Hence:

The quality of a musical sound is due to the presence of overtones in addition to the fundamental (HELMHOLTZ).

The quality as perceived by our ears varies according to the relative amplitudes of the different overtones.

For the above reason particular importance attaches to the series of notes whose frequencies are in the ratio of the whole numbers 1 : 2 : 3 : 4, &c. This is called the **harmonic series**. Beginning with the fundamental C it consists of the following notes:

1	2	3	4	5	6	7	8	9	10	11	12
C	c	g	c'	e'	g'	i'	c''	d''	e''	k''	g''

Of these the seventh and eleventh do not belong to the ordinary musical scale, and are therefore designated by special letters.

It is found that the *phase differences* of the overtones do not affect the quality. Thus it is not the actual form of the vibration, but only its composition from partial vibrations, which determines the impression upon the ear.

The composition of the musical sounds from different sources and the consequent quality will be discussed further in the next paragraph.

5. Sources of Sound

1. Application of Resonance in Acoustics.—For the production of sound, use is generally made of solid bodies whose vibrations are transmitted to the surrounding air. The amplitudes of the vibrations of these bodies are usually very small and, since the density of the air is very small, the amount of energy transmitted is also small. Hence the intensity of the sound is only slight. In order to set greater masses of air into vibration, the source is therefore coupled in most cases with a system having a large area or a large volume. This produces the desired pressure variations in the air on account of its own forced vibrations. When the coupling is very loose, we have the case of the exciter and resonator already discussed. If the damping is slight the resonance curve (fig. 17, p. 198) rises to a sharp peak; such a resonator only amplifies its own natural frequency. It must be tuned exactly to the exciter in order to produce the maximum effect. This kind of amplification by resonance is used for all sources of sound in which the main object is the production of one single note.

Coupling in acoustic processes can be observed as follows:

Two similar strings are stretched upon the monochord in such a way that the pitch, i.e. the frequency, of both is exactly the same. Then when one string is plucked, it is observed that the other is also set into vibration. The amplitude of the second string increases rapidly, while that of the first decreases at the same rate. The process is then reversed, and the second string gives back its energy to the first and comes to rest. Several such alternations can often be observed, but owing to losses of kinetic energy to the air the amplitudes of both strings soon become so small that the effect is no longer visible. In this experiment the coupling is partly through the base of the monochord and partly through the air between the strings.

By a suitable arrangement the coupling can be produced by the air alone.

When a sounding tuning fork is held near an open piano whose dampers have been raised by depression of the pedal, that string begins to sound whose

frequency coincides exactly with the frequency of the tuning fork. If the difference of frequency is slight a weak resonance may occur, but with greater differences there is no response.

When it is desired to amplify a number of different notes with different frequencies (e.g. in the case of a violin, piano or loud-speaker), the source of the note must be coupled with a system (the sound box or board) which is incapable of resonance within the range of frequencies to be amplified, i.e. which has no natural frequency in this range. In this case, the coupling must also be made as tight as possible so as to force the vibrations of the exciter upon the system (when the coupling is tight, any resonance maxima which may be present are also flattened).

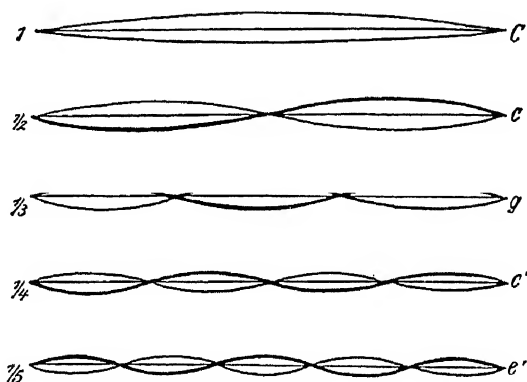


Fig. 7.—Modes of Transverse Vibration of a Stretched String giving its Fundamental and First Four Overtones

The resonance system used to amplify the sound has a considerable influence upon its quality; for as a rule the different partials are amplified to different extents, so that the ratio of the amplitudes of the overtones, which determines the quality, is altered. This effect may be desirable in many cases, but undesirable in others. Upon this depends to a great extent the difference between good and bad musical instruments. Examples of this will be given below (e.g. figs. 10, 20, 21, pp. 260 and 263).

2. Vibrating Solids as Sources of Sound: Transverse Vibrations of Strings.—In the transverse vibrations of a stretched string fixed at both ends there is always a node at each end (p. 238). Such a string can be made to vibrate either by plucking it or by bowing it with a violin bow previously rubbed with rosin. According to the nature of the plucking or bowing the string either vibrates with a single antinode in the middle (fig. 7, 1) or in the other ways shown in fig. 7, i.e. either with 1 section or with 2, 3, 4, 5 or more equal sections. Vibration in sections can be favoured by lightly touching the points which

are to become nodes, while the string is being bowed. Thus a string can give a series of higher notes (overtones) in addition to its fundamental.

From fig. 7 it follows further that the pitch of the note produced when there is one node in the middle is the same as that which would be produced if only one half of the string were to vibrate. Hence, if the fundamental note is C, the first overtone is c, i.e. the next note of the harmonic series. The higher overtones also coincide with notes of the harmonic series. Fig. 7 shows the modes of vibration of the string in producing its fundamental C and the first four overtones c, g, c' and e'. The higher overtones are particularly easily brought out if the string be bowed near one end and a point not far away

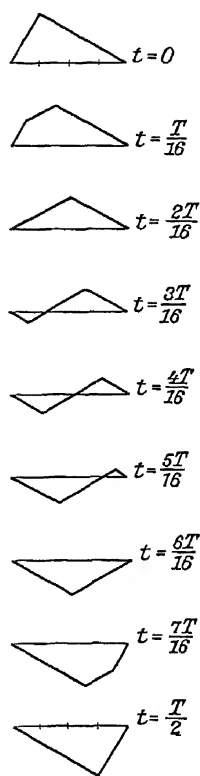


Fig. 8. — Successive Shapes of a String plucked one quarter of the way from one end.

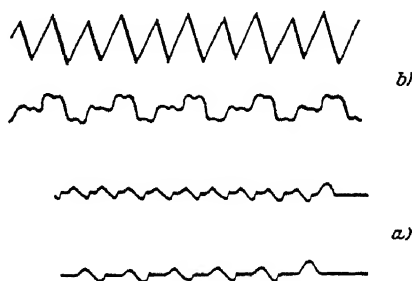


Fig. 9.—Modes of Vibration of a Point of a String (a) when Struck and (b) when Bowed

touched lightly with the finger. The positions of the nodes and antinodes can be made visible by placing small paper riders upon the string. At the nodes these riders remain in position; at the antinodes they are thrown off.

According to the formula given on p. 228 the pitch varies with the length, tension, thickness and density of the string.

Usually all the modes of vibration of the string are produced simultaneously, and are superimposed. The quality or timbre of the sound then varies according to the relative amplitudes of the different overtones. The form of vibration and hence also the quality are found to depend considerably upon the nature of the excitation (bowing of a violin, plucking of a guitar, percussion of a piano). Fig. 8 shows (as it were cinematographically) the form of vibration of a string plucked one-quarter of the way from one end. Fig. 9 (like fig. 6, p. 256) shows the vibration of one point of the string: (a) when the string is struck, and (b) when bowed.

Since strings only have a small surface area, the transmission of energy to the air is extremely slight. They must therefore be coupled

to a resonator. But this changes the quality. Fig. 10 shows the composition of the quality of a good and a poor violin from the overtones. It is remarkable that in two of the cases in the figure the fundamental note is very weak.

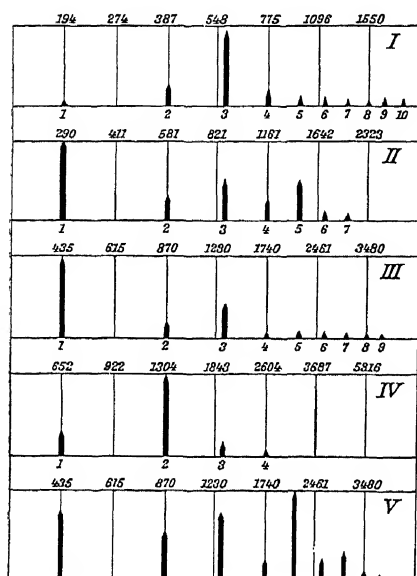


Fig. 10.—Composition of the Sound of a Stradivarius Violin (I-IV) and an Ordinary Violin (V)

I = G-string, II = D-string, III = A-string, IV = E-string, V = A-string. (The upper numbers give the frequencies in hertz, the lower numbers mark the successive members of the harmonic series.)

Transverse Vibrations of Rods.

—Vibrations may be excited in an elastic steel rod when it is supported either at both ends or in the middle or at any other points. The points of support become nodes. A straight homogeneous rod vibrates most easily when it is supported as in fig. 11. The nodes then lie one-sixth of the length of the rod from each end; in the middle and at both ends are antinodes. Other modes of vibration may be produced, but they can only be brought out fully by means of special external constraints.

Vibrating rods are used for producing chimes with such instruments as the crescent (Turkish), in musical boxes and children's glass-rod pianos, and in the xylophone. In the last named a row of tuned wooden rods is placed upon two bundles of straw laid upon the table at such an inclination to each other that

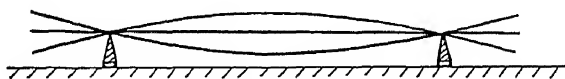


Fig. 11.—Transverse Vibration of an Elastic Rod

they come under the nodes of the rods. In these instruments the rods are struck in the middle with small hammers.

Tuning Forks (fig. 12) are very important. They consist of bent rods which vibrate transversely. They may either be struck with a *soft hammer* or made to sound by bowing them. Antinodes are formed at both ends of a tuning fork (fig. 13); the ends move inwards or outwards simultaneously. Near the bend and equidistant from the

middle of the fork are two nodes. At the middle there is always an antinode.

The tendency of a tuning fork to form an antinode at the middle of the bend is not eliminated by providing it with a rod or stem which is held in the hand. Thus the stem of the fork also vibrates, in this case longitudinally.

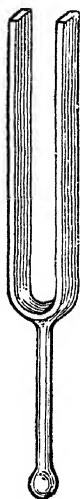


Fig. 12
Tuning Fork

When the tuning fork is held with the end of its stem against some large surface such as a table, the stem imparts periodic impulses to the table and thus sets it vibrating also with the same frequency, i.e. the same pitch, as the fork itself. The note of the fork thus becomes distinctly audible when the stem is placed against the table. At each up and down movement of the stem the table takes up a considerable part of the kinetic energy of the fork; hence the fork comes to rest much more quickly than if it is merely held in the hand.

For physical experiments the stem of the tuning fork is fixed to the upper surface of a hollow wooden box (the sounding box) (fig. 14). The top of the box performs forced vibrations owing to its coupling with the stem. The air in the box is also set vibrating with the same frequency and consequently the note of the fork is amplified.

Since the fork only gives one note, the sounding box (resonance box) is chosen so that its natural frequency is identical with that of the fork. (For a box closed at one end the length of one side must be about $\frac{1}{4}$ of the wave-length λ of the note in the air. For a box open at both ends, the length must be $\frac{1}{2}\lambda$.)

The frequency of a tuning fork is determined by the mass and the elastic restoring force. As in the case of all vibrations, the period increases as the mass increases and as the restoring force decreases. Thus the pitch of a tuning fork is lowered when the mass of the moving parts is increased, e.g. by sticking wax on to one or both prongs. The effect is determined by the moment of inertia of the wax about the nodes; consequently the nearer the wax is to the free ends of the prongs, the greater the lowering of the pitch.

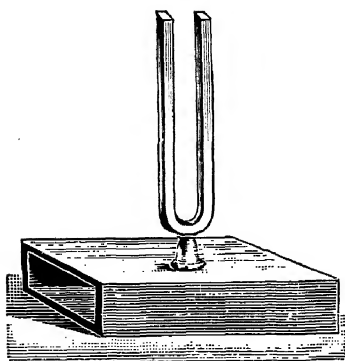


Fig. 14.—Tuning Fork with
Resonance Box

The mass of the moving parts is diminished by filing away the prongs. This therefore raises the pitch. On the other hand, if the fork be filed thinner in the neighbourhood of the nodes,

the restoring elastic force is made smaller and the pitch lowered. It is possible to make two tuning forks of identical pitch, the one long and thick and the other short and thin. The energy of vibration, however, is greater for the larger and thicker fork because its mass is greater. Hence very heavy forks

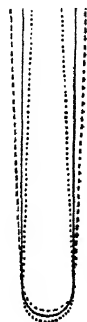


Fig. 13
Mode of
Vibration
of a Tun-
ing Fork.

Fig. 15
Tuning
Fork of
High Pitch.

(fig. 15) are used for the production of high notes of sufficient loudness and duration.

Since transversely vibrating rods usually only give their fundamental (fig. 7, p. 258), tuning forks are of considerable importance for scientific purposes on account of their purity of tone.

Transverse Vibrations of Membranes and Plates.—The two-dimensional analogue of a string is a *membrane*, artificially stretched so as to be capable of vibration. The two-dimensional analogue of a rod is a *plate*, whose capacity for vibration is due to its elasticity.

A square plate of glass or metal of uniform thickness, fixed at its middle point, can be set into vibration by bowing its edge. In this way stationary waves are formed over the whole of the plate. The state of vibration can be observed well by sprinkling fine sand upon the sounding plate. This is driven away from the places of maximum motion and piled up at the places of zero motion. In this way the

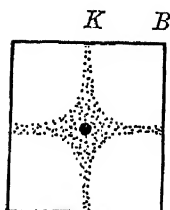


Fig. 16

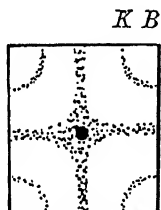


Fig. 17



Fig. 18

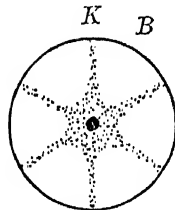


Fig. 19

Chladni Figures

nodal lines separating the antinodes are made visible. The regions on opposite sides of a nodal line vibrate with opposite phase. The patterns obtained are called CHLADNI * figures.

The formation of certain nodal lines can be favoured by touching the plate lightly at one or two points while it is being bowed. Figs. 16, 17 and 18 show the simplest figures in the case of a square plate held in the middle. Each figure corresponds to a certain note. The more complicated the figure, i.e. the larger the number of nodal lines, the higher the corresponding note. The higher notes are not harmonics of the fundamental.

The form of the Chladni figures is altered if the plate is held at some other point instead of its middle.

Circular plates usually divide up into an even number of vibrating sectors separated by radial nodal lines (fig. 19). The most readily formed pattern has six sectors.

Bells are curved plates. When struck they divide up, like circular plates, into a number of sectors with a common point at the point of suspension. If a wine-glass partially filled with water is bowed at the rim, the formation of nodes and antinodes can be observed from the

* ERNST FLORENS FRIEDRICH CHLADNI (1756–1827), born in Wittenberg, died at Breslau; he started as a jurist, but later devoted himself wholly to his favourite science, acoustics, which he enriched with many new discoveries.

fact that the water is disturbed to different extents at different points of the side of the glass.

The overtones of plates and bells are not as a rule harmonics of the fundamental. The art of bell-casting is to produce as many *harmonic* overtones as possible, and to avoid any which are not harmonic by suitable choice of size and thickness.

The vibrations of membranes and plates have recently come into importance on account of their extensive application in gramophones and loud-speakers. In this case the membranes and plates are not made to perform their own natural vibrations, but are only used for the transmission of forced vibrations to the air. Thus it is important that all the frequencies of the exciter shall be amplified to the same degree. Since, however, the amplification is greater for a natural

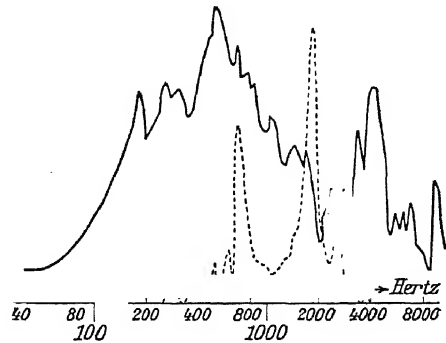


Fig. 20.—Curves showing the Reproduction of a "Good" (continuous line) and "Bad" (dotted line) Loud Speaker

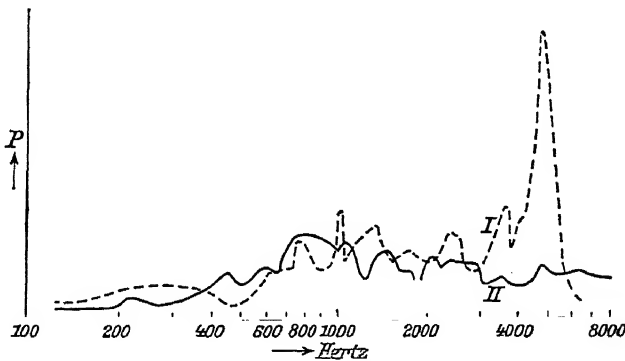


Fig. 21.—Curve showing the Reproduction of a Large Loud Speaker (II is an improved version of I)

frequency of the membrane or plate than for other frequencies (fig. 17, p. 198), care must be taken to choose the shape, material and method of fixing so that the natural frequencies are repressed as much as possible. Figs. 20 and 21 show curves in which the ordinates are the amplitudes with which different frequencies of the same original intensity are reproduced. In theoretically perfect reproduction the curve would be a straight line parallel to the axis of abscissæ.

Longitudinal Vibrations of Strings.—A stretched string can be

made to vibrate longitudinally by rubbing it with a rosined cloth. The ends of the string are always nodes. In the simplest case there is one antinode at the middle. The frequency of a longitudinally vibrating string can be calculated from Young's modulus E and the density ρ according to the formula given on p. 219, Vol. I.

In the case of the fundamental, the wave-length λ for the string is twice the length l of the string; for the distance of one node from the next is $\frac{1}{2}\lambda$. Hence, having calculated the velocity of propagation from the formula

$$v = 100 \sqrt{\frac{E}{\rho}} \text{ m. per sec.}$$

(at the place just cited it is proved that $c = 5100$ m. per sec. for a steel wire), we can also obtain the frequency from the equation

$$v = \frac{c}{\lambda}.$$

(For the general equation $c = v\lambda$, see p. 222.) Now in the case of the fundamental $\lambda = 2l$ and therefore

$$v = \frac{100}{2l} \sqrt{\frac{E}{\rho}}.$$

The frequency of a longitudinally vibrating string or wire is almost completely independent of its cross-section and its tension.

Examples.—A steel wire 1 m. long gives a fundamental of frequency 2550. In order to give the note a^1 with the frequency 435 as fundamental, a steel wire must be 5.86 m. in length.

When there is a node in the middle as well as at the ends, the wave-length is equal to the length of the wire and the note is the octave of the fundamental.

The overtones of a longitudinally vibrating wire form a harmonic series; for the distribution of nodes and antinodes is the same as that represented for transverse vibrations in fig. 21, p. 235. From the transverse vibrations shown in that figure we can construct the corresponding longitudinal vibrations by the method there shown, namely, by turning all the displacements through 90° . The maximum variations of density occur at the nodes, the minimum variations at the antinodes.

Longitudinal Vibrations of Rods.—A clamped elastic rod can be made to vibrate longitudinally by rubbing it. Metal rods and wooden rods may be rubbed with a rosined leather, glass rods with a damp cork. The point where the rod is clamped is always a node. When this point is in the middle, the free ends become antinodes. The frequency can be calculated in the same way as that already given for longitudinally vibrating strings. The overtones correspond to the odd terms of the harmonic series.

A rod clamped at one end has a node at that end and an antinode at the other. Its whole length is then a quarter of the wave-length of the fundamental. The overtones again correspond to the odd terms of the harmonic series.

If a rod is to have antinodes at the middle and at the ends, it must be clamped a quarter of the way along it from each end. The pitch is then the same as that of a rod of a quarter the length clamped at one end or a rod of half the length clamped in the middle. A rod clamped one quarter of the way along it from each end gives the purest possible note.

The electrical excitation of quartz crystals to longitudinal vibrations has recently become very important. This makes use of the property of quartz crystals of changing their length when an electric pressure is applied to the surfaces. (For further details see Vol. III.) Since it is possible to produce very pure electrical oscillations, very pure acoustic vibrations can be set up in this way. A quartz crystal in the shape of a plate or rod (*piezo-electric crystal*) is excited by an electrical oscillation corresponding to one of its natural frequencies, and is thus made to vibrate with great constancy and under certain conditions with very great intensity. (Thus, for example, from a quartz plate $10 \times 10 \times 1.6$ cm. it has been possible to send out about 1 kw. at 40,000 cycles.) Such crystals are used especially for the production of very high frequencies (up to several million cycles).



Fig. 22.—Kundt Dust Figures (seen from above)

3. Columns of Air as Resonators and Sources of Sound: Natural Frequencies of Air Columns.—Like the solid bodies discussed in the preceding section, air columns also possess certain natural frequencies. When they are excited, stationary longitudinal waves are formed.

The proof of the formation of stationary waves can be obtained as follows (KUNDT,* 1866). One end (in fig. 22 to the left) of a horizontal glass tube is closed by a movable airtight piston. Into the other end projects a rod of glass (or metal) clamped at the middle. A small light disc of cork is attached to the end of the rod within the tube. The rod is now made to vibrate longitudinally by rubbing it with a damp cork. Its ends become antinodes and the cork disc is moved backwards and forwards, thus imparting a regular succession of impulses in the form of sine vibrations to the air column enclosed in the tube. The piston at the other end of the tube is adjusted until at a certain position the note of the glass rod is considerably amplified. The air in the tube has then been set into stationary vibration, and has itself become a source of sound.

In order to investigate the nature of the vibrations of the air column, fine cork dust is sprinkled in the tube (Kundt's method). At resonance the dust piles up into peculiarly striated heaps; for, like the sand in the case of Chladni figures, it is driven away from the antinodes and collects at the nodes. The wave-length in the air column can be measured off from the positions of the heaps. Comparison with the length of the exciting rod then gives the ratio of the velocity of propagation in air and in the material of the rod.

If the tube be filled with some other gas, the wave-length is different because

* AUGUST KUNDT (1838-94), Professor of Physics at Bonn.

the velocity of propagation is different. For this velocity c is given by Laplace's equation (p. 231)

$$c = \sqrt{\frac{\gamma p}{\rho}},$$

whence it follows that for constant γ the velocities of propagation and hence also the wave-lengths for two gases are in the inverse ratio of the square roots of the respective densities, i.e.

$$\lambda_1 : \lambda_2 = \sqrt{\frac{1}{\rho_1}} : \sqrt{\frac{1}{\rho_2}}.$$

Now the densities are proportional to the molecular weights μ_1 and μ_2 . Consequently

$$\lambda_1 : \lambda_2 = \sqrt{\frac{1}{\mu_1}} : \sqrt{\frac{1}{\mu_2}}.$$

On the other hand, the method can be used to determine γ (p. 231) in the case of gases of different γ and known density.

Vibrations of an Air Column Free at Both Ends (Open Pipe).—

In this case the ends become antinodes, since the air can move freely there. In the simplest case there is one node at the middle, where the air therefore remains at rest. Here occur the maximum variations of pressure (p. 235), while at the ends the pressure variations are a minimum (because the pressure differences can become equalized towards the outside).



Fig. 23
Position
of the An-
tinode in
an Open
Pipe.

Investigation of the Motion of Air vibrating in Pipes.—Use is made of a pipe with a glass side (fig. 23). The pipe is excited in some way (see p. 270) and, while it is sounding, a light frame covered with very thin paper is lowered down into it upon a thread. A few grains of sand, previously placed on the paper, remain at rest in places where the air is at rest, but dance up and down in a lively manner where the air is in motion. When the pipe is giving its fundamental the minimum motion is found at the middle and the maximum motion at the open ends.

The pressure conditions can be investigated (after KUNDT) with the help of a water manometer of the type shown in fig. 24. The two openings are provided with small valves made of thin paper or rubber. The valve on the left opens outwards, i.e. under the influence of external rarefaction of the air, and shuts under the influence of external compression. The other valve opens inwards, i.e. under the influence of external compression. The manometer is lowered into the sounding pipe upon a thread, as in the case of the light frame in fig. 23. At the antinodes the water levels in both limbs remain the same; this occurs, for example, at the open ends of the pipe. But at the node (in the middle of the pipe) the manometer indicates a pressure difference of several

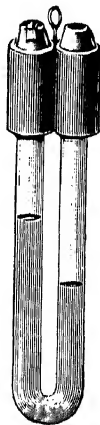


Fig. 24
Kundt Ma-
nometer

centimetres. (Differences of 30 cm. water have been observed.) Thus it is seen that the maximum pressure changes occur at the nodes.

In order to detect rapid variations of pressure use may be made of KÖNIG'S* manometric flames. This device is shown in section in fig. 25. Coal gas enters below on the right and passes through the right-hand compartment of a small chamber to the jet above where it burns. The two compartments of the chamber are separated by a thin membrane of paper or rubber. So long as this membrane is at rest, the flame is steady; but when the membrane vibrates, periodic pressure variations are set up in the right-hand compartment containing the coal gas and consequently the flame flickers with the same frequency. When viewed in a rotating mirror (fig. 26) the image of the flame is drawn out laterally into a band showing the individual flickers. Fig. 27 shows the appearance of the flame in the mirror when the membrane is under the influence of simple vibrations, which are caught in a trumpet (see fig. 25, on the left). Such manometric flames can also be brought up directly in front of holes in a sounding pipe and the corresponding pressure variations observed.

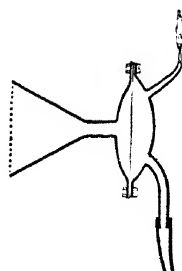


Fig. 25.—König's Manometric Flame

The pressure conditions and the positions of nodes and antinodes in an air column in stationary vibration can be well demonstrated by means of the so-called *wave tube* shown in fig. 28. This is a thin-walled iron tube with a row of holes in the top. It is closed at one end with a thin membrane and at the other with a cork. Coal gas is conducted into the tube and can be ignited at the holes so as to give a row of small flames of equal height. The resonance box of a loudly sounding tuning fork is now brought near the membrane, or a pipe is made to sound there. As a result the flames burn with different heights and produce the result shown in the figure. Each flame performs the same flickering motion as a König manometric flame. The greatest flickerings, i.e. the tallest flames, are produced at the places of maximum pressure variation, that is to say, at the nodes.

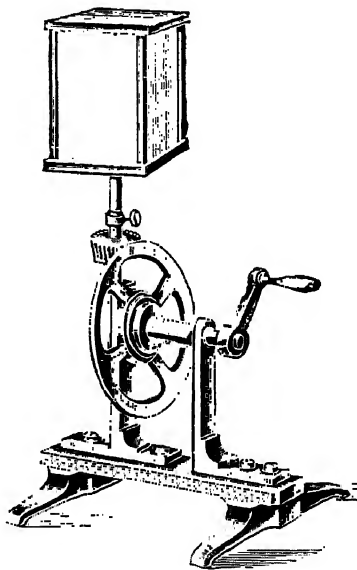


Fig. 26.—Rotating Mirror

The states of pressure and motion in the interior of a sounding pipe have been investigated often and with great care. It has been found that:

When an open pipe is giving its fundamental, a node or position of minimum motion and maximum pressure variation is formed at the middle and antinodes or positions of maximum motion and minimum pressure variation at the ends.

* RUDOLF KÖNIG, born 1832 at Königsberg, died 1904; from 1852 onwards in Paris. A mechanic, he rendered valuable service in acoustics by the construction of suitable apparatus and by his own scientific researches. His workshops are run to-day by CARPENTIER.

Excitation of Vibrations in Air Columns.—Stationary longitudinal waves can be produced in a column of air by any periodic movement whose frequency coincides with one of the natural frequencies of the column. Two types of excitation are of special importance: firstly, by means of the vibration of elastic tongues of metal (*reed pipes*), and secondly, by means of the periodic separation of vortices from a sharp edge, the “lip” (*flue pipes*).

Reed Pipes.—The air from the blower enters a chamber (fig. 35) from which its only escape is through a lateral slit. Over this slit is an elastic tongue or reed. When the velocity of the air stream is sufficiently great, the reed is swept back and closes the exit. Then when the air in the chamber has come to rest, the reed springs away again from the opening, allowing the air to flow out once more. This process is repeated in rapid succession.

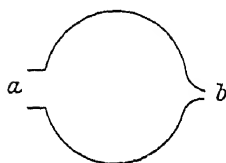


Fig. 34.—Helmholtz's Spherical Resonator

In this way the air current is periodically cut off, the frequency depending chiefly upon the natural frequency of the reed. The air vibrations thus produced serve to set up stationary waves in the pipe. It is necessary, therefore,

to tune the natural frequency of the reed to that of the pipe. For this purpose the reed is provided with a spring (see fig.) by means of which its length can be varied.

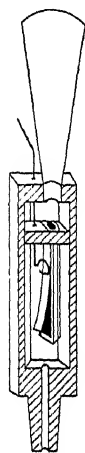


Fig. 35 Reed Pipe with Sound Horn

Air column and reed form an example of coupled systems. Actually the reaction of the former upon the latter is quite considerable, especially if the reed is very flexible. If, therefore, the natural frequencies of the reed and pipe are not exactly identical, combination vibrations are set up; in these the frequency of the reed is of the greater importance.

The reed principle is used in organ reed pipes (metallic reeds), also in clarinets, oboes and bassoons (very elastic wooden reeds). The same principle is also applied

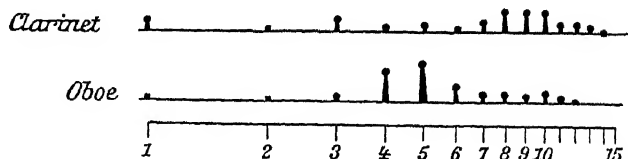


Fig. 36.—Composition of the Sound of a Clarinet, and of an Oboe

in the case of the horn and other brass wind instruments, but here the lips of the player act as double reeds opening outwards. Fig. 36 shows the composition of the sound of a clarinet and an oboe. (Abscissæ = frequencies; the numbers stand for the successive notes of the harmonic series. Ordinates = relative intensities.)

The sound of the reed itself is comparatively weak in the above cases. Reeds can be used, however, without air resonators, as in the harmonium and mouth-organ.

The Human Voice.—The human voice-organ may be regarded as a double-reed pipe instrument (fig. 37). The double reed is formed by the *vocal chords*. The air flows out through the *glottis* and sets the vocal chords vibrating. The cavities of mouth and nose act as resonators.

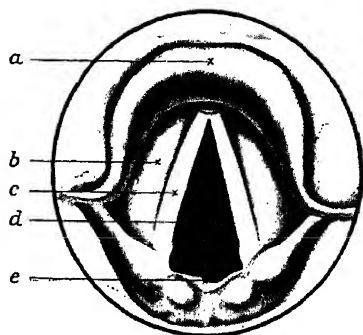


Fig. 37.—Diagram of the Larynx

a, epiglottis; *b*, false vocal chords; *c*, true vocal chords; *d*, trachea; *e*, anterior wall of the larynx.

During normal breathing the vocal chords are slack, thus leaving a wide passage for the air. In speaking they are tightened and brought nearer together, so that only a narrow space, the *glottis*, is left between them. The air driven out of the lungs flows through the glottis and thus causes the vocal chords to vibrate with a frequency that can be altered within certain limits by adjustment of their tension. The so-called *false vocal chords* (see fig. 37) also influence the vibrations of the true vocal chords, though only to a small extent. The air vibrations set up by the vibrations of the vocal chords are generally composed of very many notes. The cavities of nose and mouth act as resonators. Their shape can be regulated by suitable adjustments of the positions of tongue, teeth, and lips, and in this way the quality of the sound, i.e. the amplification of the different notes of the mixture, varied at will. The vocal chords and the adjustment of the resonance space of the mouth and pharynx are particularly important for the formation of vowel sounds (Helmholtz vowel theory). In the formation of consonants the soft palate, tip of the tongue and lips are themselves made to vibrate at different places; these vibrations produce the desired effect either alone or in combination with the complex sound given out by the vocal chords.

Each of the vowels, as sung, has its own characteristic sound composition. It is to be noted that for an adult the *absolute pitch* of the characteristic overtones is constant, since it corresponds to certain natural vibrations of the mouth cavity in the position necessary for the production of the vowel sound. Thus the frequency of the characteristic overtones is independent of the particular note upon which the vowel is sung. Vowel sounds differ therefore from the sounds of most other musical instruments in that the strength of the overtones does not depend upon their position in the harmonic series, but rather upon their absolute pitch. (HELMHOLTZ.)

Flue Pipes.—Vortices separate periodically at the surface between two layers of gas or liquid moving with different velocities. This occurs, for instance, in the case of air flowing out through a slit or nozzle. The result is a musical sound.

Ascending cigarette smoke begins to oscillate of itself after rising a short distance. Compare also the separation of vortices in fig. 68, p. 392, Vol. I. Air flowing out of a slit oscillates in the same manner. The cause of this regular periodic motion has been found to lie in the separation of vortices (p. 382, Vol. I). formed at the slit. (The same is also true of a current of gas or liquid directed

against a sharp knife edge; here too vortices are formed at the edge and separate in regular succession.) Compare in this connexion the regular flapping of a flag in a uniform wind; this is due to the separation of vortices alternately to the right and to the left.

The period of the air vibrations depends upon the width of the slit and also upon the velocity of outflow, i.e. upon the pressure of the escaping air.

If a knife edge or lip is placed in the way of the air current (as shown in fig. 39, where the lip is represented as a wedge), the air strikes in regular alternation upon the left and right sides, thus producing a note. The pitch depends upon the width and position of the lip as well as upon the size of the slit and the air pressure. The knife edge being extended upwards, periodic pressure variations are formed on both sides of it. These can be used for the excitation of stationary vibrations in an enclosed air column.



Fig. 38
Flue Pipe

By combining slit, lip and air column into one apparatus we obtain a so-called flue pipe of the type shown in longitudinal section in fig. 38. It consists

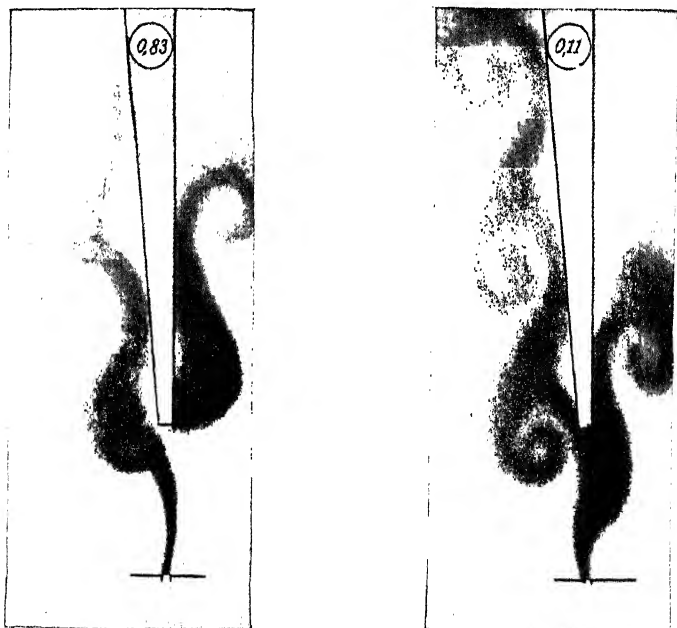


Fig. 39.—Separation of Vortices when an Organ Pipe is blown (after Carrière)
(From *Handbuch der Physik*, Vol. VIII, published by Julius Springer, Berlin)

of an air chamber K with the exit slit S, opposite which is the lip L. The air can escape between the slit and the lip. The continuation of the lip forms the resonance tube R—the actual pipe. The periodically oscillating air escaping from S strikes against the lip L and gives rise to stationary longitudinal waves in the air en-

closed in R, provided that the frequency of oscillation of the air stream coincides with one of the natural frequencies of the pipe. There is also a reaction of the stationary waves produced in R upon the frequency of the impulses of the air stream. Even if the two frequencies were not exactly in tune originally, they

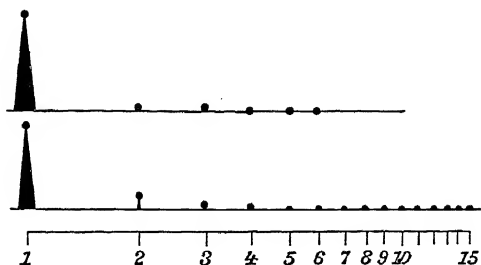


Fig. 40.—Composition of the Sound of a Flute (gently blown at medium and low pitch: medium, above; low, below)

become identical automatically. But the pipe sounds most readily when properly tuned. Hence for every pipe there is an optimum position of slit and lip.

The frequency of the pipe is raised by narrowing the slit and placing the lip nearer to it. Thus a flue pipe, which gives its fundamental when the slit is wide and the lip at a comparatively great distance from it, may give its overtones when the slit is made narrower and the lip brought nearer to it.

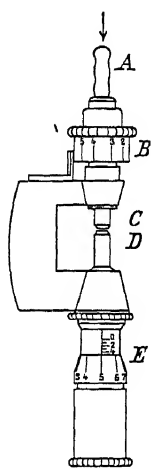


Fig. 41.—Galton Pipe

Fig. 39 shows two photographs of the processes occurring when a flue pipe is blown. Two different times during one period are depicted. (The numbers give the fraction of the period already completed.) Flue pipes are used in organs. The flute and flageolet are instruments of this type. The sounds of a flute (fig. 40) have very few and very feeble overtones and are therefore almost pure sine notes.

*Galton Pipe.**—For the production of notes of very high pitch a small flue pipe (fig. 41) may be used. Its length can be varied with micrometer adjustment at E and the relative positions of the slit C and the lip D by means of the micrometer adjustment at B. The air is blown in at A. In this way it is possible to produce frequencies as high as 30,000 cycles (per second).

Sensitive Flames.—When a current of gas is on the point of breaking up into vortices, this process can be brought about by very small external disturbances. If the pressure of gas burning at a small jet is gradually increased, the flame will begin to “roar” at a certain point. The reason for this lies in the fact that at this pressure vortex-formation sets in. When now the pressure is diminished again until the “roaring” just stops, the steadily burning flame so obtained shows a peculiar behaviour towards notes of high pitch. When such a note is sounded at a short distance, the flame at once shortens. This also occurs even if the pitch of the note lies above the upper limit of audibility. Such a flame is

* FRANCIS GALTON, born 1822 in London, died 1911, physician and meteorologist.

particularly sensitive towards rattling of glass, jingling of bundles of keys, crackling or tearing of paper, and clicking of the tongue.

Excitation of Vibrations in Air Columns by other Means.—*Singing Flames*.* A current of gas issuing from a fine jet tends to begin to vibrate. This tendency persists in the case of hydrogen or coal gas when the current is ignited at the jet so as to burn with a long thin flame. If such a flame is introduced from below into a vertical glass tube about 2 or 3 cm. wide, the tube will begin to sound when the flame has reached a suitable position. The pitch of the note depends only upon the length of the air column. In this experiment the flame itself vibrates. The periodic development of heat due to the increase and decrease of the size of the flame plays an important part in maintaining the vibrations.

A vertical tube can also be made to give a note by bringing a hot gauze under it at about a quarter of the length of the tube from its lower end.

4. Production of Sound Waves without making use of Natural Vibrations.

The Siren.—The simplest source of sound from a theoretical standpoint is the *siren* (p. 253) of CAGNIARD LATOUR.† A circular disc (fig. 42) rotates about

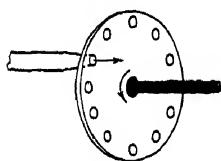


Fig. 42.—Principle of the Siren

an axis through its centre in front of the opening of a nozzle through which air is blown. The disc has a row of holes in it parallel to its circumference; as it rotates, these holes move past the opening of the nozzle. Thus the air stream is periodically interrupted. Each time a hole comes opposite the nozzle, a puff of compressed air escapes. Then when the opening of the nozzle is closed, the inertia of the moving air produces a rarefaction. These periodic pressure variations are propagated through the elastic air to our ears, where they are perceived as a musical note. If the number of revolutions of the disc per second is known, the frequency of the note is obtained by multiplying this by the number of holes.

The siren may be driven either by the air current itself (often also by a current of high-pressure steam) or else by means of an electromotor. It is often provided with a revolution counter.

All other notes produced by rotation belong to the same class. For example, the singing of electromotors, turbines and rapidly rotating aeroplane engines, the screeching of circular saws (accompanied, however, by the natural vibrations of the saw plate), &c.

Particular practical interest attaches to the *sound of aeroplanes*, which is

* This experiment is often known by the name "chemical harmonicon" because this kind of production of musical sounds was first observed in 1777 by HIGGINS during chemical experiments with hydrogen gas. The experiment can be carried out with equal success with a small coal-gas flame, especially if a small reservoir (e.g. a litre flask) be inserted between the gas tap and the jet, so as to prevent the proximity of the tap from interfering with the formation of the vibrations.

† CHARLES CAGNIARD DE LATOUR (1777–1859) first determined the frequency of a note in 1819 by means of his siren. The remarkable name "siren" is derived from the fact that the apparatus also produces musical notes under water when driven by a stream of water instead of air. This is the rather far-fetched reason for naming it after the island sea-nymphs, who sang with such bewitching sweetness to Odysseus. The siren was considerably improved by LUDWIG SÆEBECK (1805–49), grammar-school master, latterly Professor of Physics at Leipzig.

made up partly of the siren notes of the motor and propellers and partly of the "flue" notes produced by the current of air past the machine (p. 272).

The Thermophone.—This device is based upon the fact that the periodic development of heat in a very thin metal wire carrying an alternating electric current is transmitted to the surrounding gaseous medium, thus producing corresponding pressure variations. (The frequency of these variations is found to be either the same as or twice that of the alternating electric current, according to the conditions.) The thermophone, which functions very exactly and the intensity of whose sound production can be calculated, has recently found extensive application for scientific purposes.

CHAPTER II

Sound Waves. Hearing. Music

1. The Propagation of Sound

1. Velocity of Propagation.—The velocity of propagation of longitudinal elastic waves, of which sound is a special case, has already been discussed (p. 229 *et seq.*). As we have seen, the velocity of sound in solids and liquids is considerably greater than in gases. The following table gives the values for a few substances:

Hydrogen at 0° C.	1261 m. per sec.
Carbon dioxide at 0° C.	259 "
Water at 15° C.	1440 "
Sea water at 15° C.	1503 "
Aluminium	5104 "
Lead	1320 "
Cork	approx.	500 "
Rubber	50 "

The velocity of sound in normal moist air is, in metres per second,

$$c = 331 \sqrt{1 + 0.004t}$$

where t is the temperature in degrees centigrade.

The initial velocity of propagation of explosive waves is often considerably greater than that of sound. In air such initial velocities have been measured up to twice the normal velocity of sound.

2. Reflection of Sound.—The reflection of sound is governed by the same laws as have already been given (p. 216 *et seq.*) for waves. After reflection at a plane wall, the sound waves move as if they had come from a source lying as far behind the wall as the real source of the incident waves lies in front of it (acoustic image of the source). If the real source is far enough from the wall, the reflected sound (**echo**) is heard separately from the original sound. For this it is necessary that a certain interval of time shall elapse between the arrival of the two sounds at the ear.

When the source is nearer to the wall, we hear the reflected sound merely as a prolongation of the original one (**reverberation**). In closed

spaces the reverberation serves to amplify the sound, provided that it follows so rapidly as to be superimposed upon it. On the other hand, if the reverberation reaches our ear so late that it is superimposed upon a subsequent sound, the effect is to render the whole indistinct and blurred (disturbing reverberation in large churches).

We can distinguish about 10 sounds per second (compare p. 283). Hence at 17° C. the source of sound must be at least $340/10 = 34$ m. distant from its acoustic image, i.e. at least 17 m. from the reflecting wall, in order that the echo may be heard separately from the original sound.

If a source of sound is placed at the focus of a large spherical concave reflector, the reflected waves have a plane front (fig. 13, p. 218). Hence they no longer spread in all directions and can therefore travel long distances in a straight line (whispering galleries). Ear trumpets and speaking tubes also depend upon this kind of concentration of the sound energy.

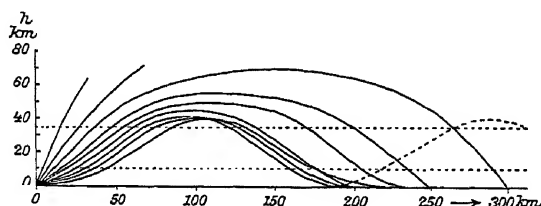


Fig. 1.—Path of Sound through the Atmosphere over Great Distances

The reflection of sound waves has found a very important practical application in the *sonic depth finder* of БЕЛМ. This is used principally for measuring the depth of the sea, which is obtained from the time taken by a sound signal to reach the bottom and be reflected back again as an echo. Very reliable results are obtained by the use of automatic time registration. With the help of this very rapid method more accurate information has been obtained about the shape of the sea bed than was hitherto possible. The procedure is also of great importance for the safety of navigation. The method is likewise used in aviation.

3. Refraction of Sound Waves.—When sound waves pass from one medium into another, a change of direction (refraction) occurs. The nature of this has been discussed fully above (p. 248 *et seq.*). It has been found possible to make large concave lenses of thin paper or rubber sheet filled with carbon dioxide, which focus sound rays in the same way as light rays are made to converge by a convex lens of glass (condenser lens).

The frequently observed anomalous propagation of sound is due to refraction through air layers of different temperature. This is the explanation of the "zone of silence" (fig. 5, p. 255). Fig. 1 represents the paths of a sound over great distances under fairly normal meteorological conditions. Attempts have recently been made to obtain information about the course of sounds and hence about the state of the upper atmospheric strata by means of artificially produced explosions.

Superposition of Sound Waves. Beats.—When two wave trains of approximately the same frequency meet, periodic intensity variations or **beats** are produced (p. 224). The number of beats per second is equal to the difference between the frequencies of the two systems. When two sources simultaneously sound musical notes of slightly different pitch, the ear perceives these periodic intensity variations as an alternation of *crescendo* and *diminuendo*. Such beats can be heard easily in the case of two similar tuning forks, one of which has been put slightly out of tune by sticking some wax on its prongs.

The formation of beats is a certain proof that two notes are approximately but not exactly in tune. Use is made of this in tuning musical instruments.

Combination Tones.—Two pure notes may give rise to further notes called **combination tones**, especially if they both exert a strong influence upon the same body—say a mass of air or a membrane. The most intense of these new notes is usually the so-called **difference tone**, which has been known for a long time.* Its pitch corresponds to the difference $n_1 - n_2$ of the frequencies of the notes producing it. The difference tone may be regarded as a beat tone. As the beats become more rapid, they eventually produce an audible note, the difference tone. The so-called **summational tone** $n_1 + n_2$ is usually considerably weaker and hardly audible. Difference tones of higher order are also often easily perceptible. The theory of combination tones has been given by H. HELMHOLTZ. They must appear whenever the amplitudes of the vibrations of the sounding body are so great that the restoring force can no longer be taken as proportional to the displacement from the equilibrium position as required by Hooke's law. If the square or higher powers of the displacement occur in the expression for the restoring force, the latter is no longer symmetrical. Combination tones may be formed at the different membranes within the ear; in this case they are not present in the outer air and cannot be amplified by means of resonators. They are therefore known as *entotic* † or *subjective* combination tones to distinguish them from the *objective* combination tones, which can be amplified by resonators.

Interference of Sound Waves.—Interference can arise by the superposition of two systems of sound waves, just as for water waves (figs. 6 and 7, p. 214). It can be recognized by the ear when the frequencies of the two notes are either identical or slightly different.

The conditions for the production of two synchronous ‡ wave systems in the air are fulfilled, for example, when a tuning fork vibrates freely.

* The violin virtuoso GIUSEPPE TARTINI (1692–1770) first discussed combination tones in 1754 in an essay; the Lobenstein organist GEORG ANDREAS SORCE had first referred to them publicly in 1744.

† Gr., *entós*, within; *ous*, *ōtos*, the ear.

‡ Gr., *syn*, together; *chrónos*, time. *Synchronous* is used in physics to describe two processes whose successive states occur simultaneously.

Two similar wave systems spread from the two prongs and produce interference. The greatest amplitude of the resultant waves formed by the superposition of the two components lies on the perpendicular bisector of the line joining the prongs. At the sides of this line of greatest amplitude lie two hyperbolic lines of minimum amplitude.

The presence of these regions of maximum and minimum loudness can be detected by the ear by walking round a sounding tuning fork or turning the fork near the ear. As the fork is turned right round once, the note is heard to increase or decrease in intensity four times. It is loudest on the perpendicular bisector of the line joining the prongs and attains another maximum of intensity upon the line joining the prongs. Between these maxima lie the four directions of minimum loudness.

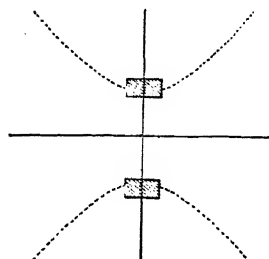


Fig. 2.—Interference Hyperbola of a Tuning Fork

In fig. 2 the shaded rectangles represent the two ends of the prongs seen in plan. The two continuous lines are the directions of maximum loudness, the dotted hyperbola branches (p. 212) the loci of the positions of minimum loudness. The form of the hyperbola depends upon the distance between the prongs of the fork and also upon the wave-length of the note.

If two tuning forks of the same pitch are made to sound side by side, new interferences are produced between the two forks as well as those due to each fork separately. Maxima of loudness are again obtained upon the perpendicular bisector of the line joining the two forks, and on each side of this there are again hyperbolic regions of minimum loudness. When the forks are at a greater distance apart several hyperbolas of maximum and minimum loudness may be formed.

The following instructive experiment upon the interference of sound waves was first described by QUINCKE;* it may also be used to determine the wave-length of a note. The tube T (fig. 3) is joined as shown to another tube which is bent round at A and B and unites again at the tube O. The one limb B of the double tube can be drawn out in the manner of a trombone. The tube T is placed before a source giving a pure note, so that the waves pass through the apparatus via both A and B to O. If the lengths of the paths traversed by the sound waves in the two limbs are equal, the two parts of the wave system reach O in the same phase and therefore combine to give approximately the original intensity. But if the variable limb be pulled out a distance d , i.e. if the path on that side be increased by $2d$, the two parts of the wave system will reach O with a phase difference. When now the path difference $2d$ is equal to an odd multiple of half the wave-length, the two parts will interfere and neutralize each other and nothing will be heard at O. On the contrary, when the path difference is equal to an even multiple of half the wave-length a maximum of loudness is heard at O.

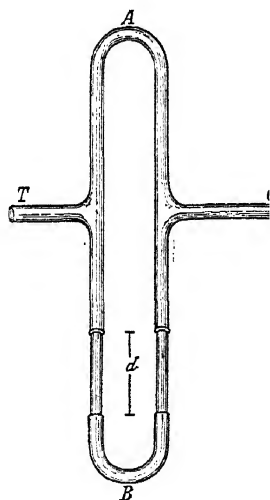


Fig. 3.—Interference Tube (after G. Quincke)

* GEORG QUINCKE (1834–1924), Professor of Physics at Heidelberg until 1908.

2. The Doppler * Effect

As a whistling locomotive, a tram sounding its bell, or a cyclist ringing his cycle bell passes us, we hear a sudden drop in the pitch of the note. These are special cases of a general effect.

When the distance between us and a source giving a note is decreasing, the pitch of the note appears to be raised; when the distance is increasing, the pitch appears to be lowered as compared with the pitch when the distance is constant.

1. **Medium at Rest Relative to the Observer.**—As the source of the note approaches our ear, the distance between the successive compressions is reduced, since the point at which the second compression is sent out from the source lies nearer than the point at which the first is sent out. The wave-length is therefore diminished as compared with the case in which both source and observer are at rest. The diminution δ is equal to the distance covered by the source during

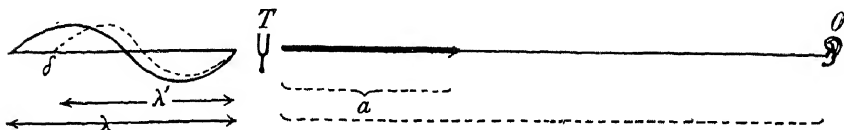


Fig. 4.—Doppler Effect; source in motion, observer at rest

one complete vibration (fig. 4). If the source T moves a distance a per second (velocity relative to the ear) and a distance δ per vibration, we must have

$$a = n\delta,$$

where n is the frequency of the note. The wave-length λ is reduced by δ to the new apparent wave-length λ' , i.e.

$$\lambda' = \lambda - \delta.$$

The apparent frequency n' is given by the relation (p. 222)

$$c = n\lambda = n'\lambda'.$$

Hence we have

$$n' = \frac{c}{\lambda'} = \frac{c}{\lambda - \delta} = \frac{cn}{n\lambda - n\delta} = \frac{c}{c - a} \cdot n.$$

If the source recedes from the ear with the relative velocity a , we have instead

$$\lambda'' = \lambda + \delta \quad \text{and} \quad n'' = \frac{c}{c + a} \cdot n.$$

As a source of sound approaches an observer its pitch appears too high; as it recedes, its pitch appears too low. At the moment of passing, therefore, the apparent pitch must fall suddenly. The interval of this fall is

$$\frac{n'}{n''} = \frac{c + a}{c - a}.$$

* CHRISTIAN DOPPLER (1803-53), Professor of Mathematics in Prague and Vienna, first enunciated the principle of this effect in 1842 in connexion with the colour of stars. He maintained that the colour of a self-luminous body (e.g. a star) must be displaced towards the blue end of the spectrum when the body is moving towards us, and towards the red end when it is receding from us. BUYS-BALLOT (1817-91) investigated the effect experimentally with moving sound sources in 1845. See also Vol. V.

Example.—Let the velocity of a cyclist be $a = 18$ km. per hr. $= 5$ m. per sec. Then

$$\frac{n'}{n''} : \frac{330 + 5}{330 - 5} = \frac{67}{65} = 1.03.$$

The musical interval through which the note of the cyclist's bell falls as he passes a stationary observer is therefore smaller than a smaller chromatic semitone (i.e. $25/24 = 1.04$). For a railway locomotive moving at 54 km. per hr. $= 15$ m. per sec. the corresponding interval is

$$\frac{330 + 15}{330 - 15} = \frac{23}{21} = 1.095,$$

i.e. somewhat smaller than a minor tone ($10/9 = 1.11$).

2. Medium at Rest Relative to the Source.—When the ear O approaches the source T with the velocity a (fig. 5), it hears not only the n vibrations sent out

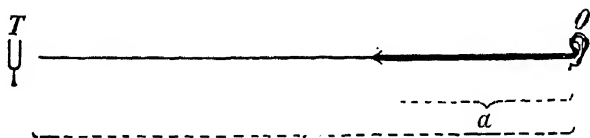


Fig. 5.—Doppler Effect; source at rest, observer in motion

from T per second but also those lying upon the path of length a which it covers. The extra number d of vibrations entering the ear per second is given by

$$d : n = a : c,$$

whence

$$d = \frac{na}{c}.$$

The apparent frequency n_1' is then

$$n_1' = n + d = \frac{c + a}{c} \cdot n.$$

When the ear recedes from the source the positive sign becomes negative and we have

$$n_1'' = \frac{c - a}{c} \cdot n.$$

Demonstration and Experimental Observation.—The change of pitch due to the motion of the source can be demonstrated by swinging a whistle round in a circle (best in the open air) upon the end of a rubber tube through which the whistle is blown. An observer standing in the plane of the circular motion hears a rise and fall of pitch every revolution.

In the case of two railway trains passing one another in opposite directions, the one whistling, an observer in the other hears at the instant of passing a change of pitch over an interval which may be as great as a third.

When a powerful tuning fork (fig. 15, p. 261) of say $n = 2000$ is made to approach a wall with the velocity $a = 1$ m. per sec., an observer situated farther from the wall hears distinct beats. These are due to the superposition of the direct and reflected waves. The former arrive at the ear directly from the fork, which is receding. The reflected waves behave as if they came from the acoustic image of the fork (behind the wall), which is approaching the ear with the same

velocity. Thus the ear hears two notes of frequencies n' and n'' . Since $c = 330$ m. per sec., $a = 1$ m. per sec., and $n = 2000$, we have

$$n' = 2006 \text{ and } n'' = 1994.$$

The ear therefore hears 12 beats per second.

3. The Human Ear

The human organ of hearing (fig. 6) consists of the external part or *pinna*, the ear canal or *auditory meatus*, the drum or *tympanic membrane*, the small bones or *ossicles* (called respectively the hammer, anvil and stirrup), the *vestibule* with the three *semicircular canals*, the spiral *cochlea* and the *Eustachian tube*.*

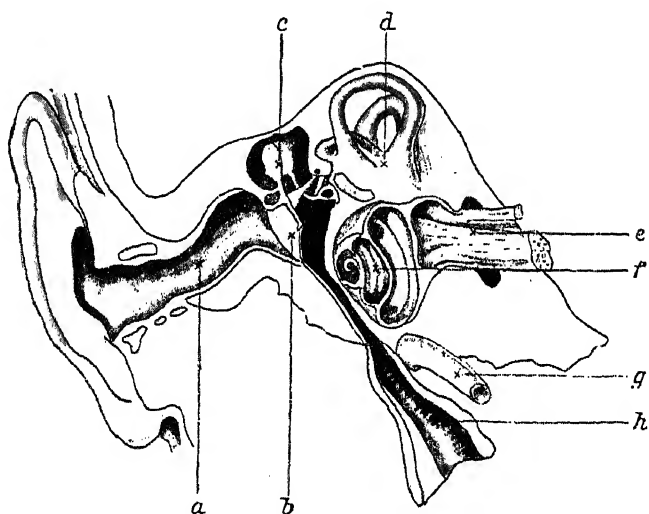


Fig. 6.—The Human Organ of Hearing (Right Ear). All Parts shown in the natural positions
a, external ear canal; *b*, drum or tympanic membrane; *c*, chain of ossicles; *d*, semicircular canals; *e*, auditory nerve; *f*, cochlea; *g*, carotid; *h*, Eustachian tube.

A musical note entering by way of the pinna and ear canal produces vibrations of the tympanic membrane; these are then transmitted by the ossicles to the oval window of the vestibule. The labyrinth, consisting of the vestibule, semicircular canals and spiral cochlea, is filled with a fluid, which is thus also made to vibrate. The cochlea is divided by a partition into two hollow spaces lying one above the other, and known as the *scala vestibuli* and the *scala tympani*. This partition is composed of a bony projection from the axis of the cochlea, joined at the outside to a membrane; it is the part of the ear which really receives the sound. The membrane part of the partition and

* So called after the physician BARTOLOMMEO EUSTACHIO (born 1574 in Rome), who gave an accurate description of the ear.

also a system of extremely fine hairs (Corti's* organ) are set into vibration by the vibration of the fluid filling the inner ear. The different hairs of Corti's organ and the membrane of the partition are of different length and thickness (the number of hairs is about 5000) and thus resound to different frequencies. The ends of the individual nerve-fibres of the auditory nerve are attached to the ends of the individual hairs. Thus when a note of a certain pitch strikes the ear, it is transmitted through the ossicles and the fluid of the inner ear to the membrane and sets a definite hair of Corti's organ vibrating (probably by vortex formation in the surrounding fluid). The nerve fibre attached to the end of the vibrating hair then transmits the excitation to the brain (resonance theory of audition).

The semicircular canals lie in three mutually perpendicular planes. They are assumed to give us our sense of direction in space (upwards, forwards, sideways) and our capacity for preserving our equilibrium. The otoliths (bony concretions in the membranous labyrinth) probably have a similar function.

The *range of audibility*, both from the point of view of frequency and of loudness, is shown in fig. 1, p. 252. The upper pitch limit of audibility varies for different individuals. It decreases with increasing age: at 20 years old it is about 19,000, at 35 about 15,000, and at 47 about 13,000 vibrations per second. Thus old people can no longer hear such sounds as the chirping of crickets or the squeak of bats.

According to fig. 1, p. 252, the *greatest sensitivity* of the ear for small sound intensities lies at a frequency of about 2300 hertz. This sensitivity is extremely high. The minimum pressure variations of about $7 \cdot 10^{-4}$ dynes per cm.^2 are less than 10^{-9} atm.; thus the ear can detect air vibrations whose amplitudes are much smaller than one atomic diameter (10^{-8} cm.) (M. WIEN).

Experienced musicians are also extremely sensitive to small differences in pitch between two notes. In order that they may be recognized as out of tune, the frequencies of two notes (of medium average pitch—500–2500 hertz) need only differ by a fraction of 1 hertz. The minimum perceptible difference of pitch is found to be independent of the absolute pitch over a wide range.

Our comparatively certain sense of the *direction* from which a sound reaches us probably depends on our extreme sensitivity to differences in the time of arrival at our two ears. When this difference is less than 0.00003 sec. the source of the sound seems to be in the plane bisecting at right angles the line joining our ears. But if the difference is greater than this minimum, the source is recognized as being more or less to the side, according to the magnitude of the difference. The impression of maximum lateral position of the source (i.e. 90° to the right or left) corresponds to a time difference of 0.0006 sec. This impression remains for all greater differences. The lower limit 0.00003 sec. corresponds to a sound path of 1 cm.; the upper limit 0.0006 sec. to a path of 21 cm. If the sounds are not of short duration (clicks or pops) but sustained notes, the impression of direc-

* First described in 1851 by Marchese ALFONSO CORTI (1822–76). CORTI took his doctorate in 1847 at Vienna, later carried out anatomical investigations of the inner ear at Wurzburg, but had to give up science on account of illness, and devoted himself from 1852 onwards to agriculture in his native country, Italy.

tion is determined apparently by the time difference between the arrival of the same phase at the two ears. Thus notes with wave-lengths shorter than 1 cm. would not convey any sense of direction, if they were audible. As a matter of fact the highest audible notes (chirping of crickets) can only be localized with the greatest difficulty, whereas for notes of medium pitch the direction can be determined correct to about 3° . If a signal of short duration (a click) arrives at one ear more than $1.2 \cdot 10^{-3}$ sec. later than at the other, it is heard twice. Thus unconsciously (i.e. as direction) we can recognize time differences as low as $3 \cdot 10^{-5}$ sec. with our ears; consciously, as low as $1.2 \cdot 10^{-3}$ sec.

4. Theory of Music

Consonance, Dissonance, Triad.—The impression produced by sounding two musical notes together may be pleasant or unpleasant, according to the particular notes chosen. In the first case we say that the notes are **consonant**, in the second case **dissonant**. In the former class we may quote the octave (C-c), fifth (C-G), fourth (C-F), major third (C-E), and minor third (E-G). The pairs of notes given in brackets are examples of the respective consonances. Other examples of a fifth are (E-B) and (F-c). The second (C-D) and the seventh (C-B) are the chief examples of dissonances. Comparing the ratios of the frequencies in consonant pairs we arrive at the following general law:

The ratio of the frequencies of two consonant notes can be expressed as the ratio of two small whole numbers. The smaller these numbers, the more complete the consonance. (Pythagorean school about 500 B.C.)

According to HELMHOLTZ the dissonance of two notes is due to the effect of beats, which (like all intermittent stimuli, such as the flickering of light, scratching and the like) cause an unpleasant sensation. The feeling of dissonance is no longer produced if the beats are slow enough to be recognized as separate disturbances, nor if their frequency exceeds a certain limit. In the latter case, as for rapidly intermittent light like an arc or filament lamp lit with an alternating current of high enough frequency, the variations become too rapid to tire the nerves and the notes blend to a *consonant* mixture. The beats formed by the superposition of the many overtones may also cause dissonance in the case of two or more musical sounds. In the same way the higher harmonic overtones (the interval between which decreases as we pass up the harmonic series) or the presence of inharmonic overtones may impart a dissonant character to a single musical sound. Bells may show markedly inharmonic overtones (p. 263).

Arranging the consonances according to the magnitude of their intervals, we obtain:

C-c	..	octave	..	1 : 2
C-G	..	fifth	..	2 : 3
C-F	..	fourth	..	3 : 4
C-A	..	sixth	..	3 : 5
C-E	..	major third	..	4 : 5
E-G	..	minor third	..	5 : 6

The reason why the boundary between consonance and dissonance lies at the number 7 may perhaps lie in the fact that this number does not correspond to any note used in music. Thus because the intervals 6 : 7 and 7 : 8 do not exist, the gap between the intervals 5 : 6 and 8 : 9 is particularly wide. The interval 5 : 6 is reckoned (nowadays) among the consonances, but 8 : 9 among the dissonances.

If several notes are to be consonant, each pair of them must also be consonant. The most complete consonance within the range of an octave is the **major triad** or **common chord**

$$C-E-G = 4 : 5 : 6.$$

Adding the octave of the ground note or tonic we obtain the consonance

$$C-E-G-c = 4 : 5 : 6 : 8.$$

The consonant intervals in this are the octave, fifth, fourth, major third and minor third.

If to this major triad we add above the further major triad formed of the notes G-B-d and below the further major triad formed by the notes F₁-A₁-C, we obtain the sequence

$$F_1-A_1-C-E-G-B-d,$$

which contains all the notes of the major scale or their higher or lower octaves. (Construction of the scale according to CHLADNI, p. 262.)

Minor Scale.—The scale given above is the major scale. The chief difference in the **minor scale** is that the third note is replaced by a somewhat lower note at the interval 6 : 5. Thus in the bottom line of the table on p. 253 the frequency 30 (*re*) must be replaced by 28.8. In the minor scale the sixth and seventh notes are also lowered.

The Major Scale with Arbitrary Tonic.—In playing a piano it is desirable to be able to produce a major scale starting from any note. Thus, for example, it is desirable that the series of numbers 24, 27, 30, &c., proportional to the frequencies shall correspond to actual notes of the piano when we start at D instead of C. The intervals 8 : 9 and 9 : 10 are so nearly equal that they can only be distinguished with difficulty (p. 254). Thus the major scale with D as tonic can be started with the notes D, E. The next note must be such that the ratio of its frequency to that of E is either 9 : 8 or 10 : 9. This note does not exist in the major scale of C. It must be higher than F and lower than G. Its frequency can be found by multiplying that of D (namely 27) by 5/4 (interval of the major third). In this way we obtain the frequency 33.75. Proceeding farther, it is found necessary to insert another new note between c and d; for in the major scale of D the seventh note (with the interval 15/8 from the ground note 27) corresponds to a frequency of $27 \cdot 15/8 = 50.63$. This lies between c (48) and d (54).

Starting from the other notes as tonics and forming major scales, we come to the result that new notes have to be inserted between each of the pairs of consecutive notes of the scale C D E F G A B c. This is done by multiplying the frequency of the next lower note by $25/24$ (the note so obtained is known as the *sharp* and is indicated by the symbol #) and that of the next higher note by $24/25$ (the note so obtained is called the *flat* and is indicated by the symbol ♭). Thus the notes obtained by sharpening the notes of the major scale of C are: C#, D#, E#, F#, G#, A#, and B#. Those obtained by flattening are: C♭, D♭, E♭, F♭, G♭, A♭, and B♭. The calculation does not give identical frequencies for such pairs as C# and D♭, the former of which has the frequency 25.0 and the latter 25.92. But since these two frequencies only differ slightly, they are replaced by a single note lying between them in the case of instruments (such as the organ and piano) which only have fixed notes. This compromise gives a new note which bears both names C# and D♭.

Equalization of Intervals.—A musical error is introduced by inserting only *one* note instead of *two* between C and D, D and E, F and G, and A and B. In order to make this error as small as possible in instruments with fixed notes (e.g. piano, harp and organ), it is spread out over all the notes of the octave by making all the intervals (12 in number) of the octave exactly equal. This is done by dividing up the octave interval (2 : 1) into twelve equal intervals, each having the value $\sqrt[12]{2} : 1 = 1.0595 : 1$. The scale so obtained is said to be **equally tempered**. In it the interval C–D is $(\sqrt[12]{2})^2 = 1.1225$, instead of $27/24 = 1.1250$ as in the natural scale. The complete scale of 12 semitones is called the **chromatic scale**.

In instruments (such as the violin, whose “open” strings give the notes g, d, a¹ and e¹) where the notes are not fixed, the player tunes his notes by ear by pressing his finger on the string so as to mark off a certain suitable length. When playing alone without piano accompaniment, a violinist plays natural (i.e. not tempered) notes; but when playing together with a piano or organ he must temper his scales equally so as to match the fixed notes of the accompanying instrument.

The tuning of a musical instrument with fixed notes is performed as follows. The note a¹ is first tuned correctly with the help of a standard tuning fork (435 vibrations per second, French pitch). The remaining notes are then tuned by ear to the right intervals, proceeding upwards and downwards from a¹ by fifths. A correction must subsequently be applied, because proceeding in fifths does not give exactly the same result as proceeding in octaves. Thus the seventh octave with the interval $2^7 : 1 = 128 : 1$ differs from the twelfth fifth with the interval $(3/2)^{12} : 1 = 129.7 : 1$. The tuning by fifths is therefore corrected subsequently, so that the highest note a^{III} exactly coincides with the seventh octave of the lowest note A₁₁. The octaves are made pure, because our ear is much more sensitive to impure octaves than to impure fifths. The impure but equally tempered fifth has the interval $(\sqrt[3]{2})^7 : 1 = 1.498 : 1$ instead of $1.5 : 1$, as in the natural scale.

The equally tempered tuning of an instrument with fixed notes can only be performed by persons who by long practice have attained the musical ear for this temperament, analogous to the natural musical ear for untempered intervals.

RELATIVE AND ABSOLUTE FREQUENCIES OF THE NOTES
OF THE UPPER OCTAVE

	Relative Frequencies		Absolute Frequencies of the Notes of the Upper Octave (a' = 435)
	Natural Tuning	Equally Tempered Tuning	
c	1.00000	1.00000	258.652
c \sharp	1.04166 \}	1.05946	274.033
d \flat	1.08000 \}		
d	1.12500	1.12246	290.327
d \sharp	1.17187 \}	1.18921	307.592
e \flat	1.20000 \}		
e	1.25000 \}	1.25992	325.881
f \flat	1.28000 \}		
e \sharp	1.30208 \}	1.33484	345.259
f	1.33333 \}		
f \sharp	1.38889 \}	1.41421	365.730
g \flat	1.44000 \}		
g	1.50000	1.49831	387.541
g \sharp	1.56250 \}	1.58740	410.585
a \flat	1.60000 \}		
a	1.66667	1.68179	435
a \sharp	1.73611 \}	1.78180	460.866
b \flat	1.80000 \}		
b	1.87500 \}	1.88775	488.271
c \flat	1.92000 \}		
b \sharp	1.95313 \}	2.00000	517.305
c	2.00000 \}		

TABLES

TABLE I.—THERMAL CONSTANTS

Solids	Coefficient of Linear Expansion (about 18°) $10^{-6} \times$	Specific Heat (cal./deg. gr.)	Atomic Heat	Melting-point, °C.	Latent Heat of Fusion (cal./gr.)	Thermal Conductivity (cal./deg. cm. sec.)
Aluminium ..	21.8	0.214	5.8	658	80	0.48
Bismuth ..	13.4	0.029	5.9	271	13	0.019
Brass ..	18.0	0.093	—	900	—	0.15–0.30
Cadmium ..	28.6	0.055	—	321	14	0.22
Carbon (amor.)	—	0.26	3.1	3000 (subl.)	—	0.01 (graph.)
Copper ..	15.9	0.091	5.7	1083	42	0.90
Glass ..	8.0	0.190	—	800–1400	—	0.0023
Gold ..	14.0	0.031	6.7	1063	—	0.70
Iron ..	12.0	0.105	5.6	1100–1600	30	0.14–0.17
Lead ..	28.8	0.031	6.4	327	5.5	0.08
Magnesium ..	25.0	0.250	6.0	651	46	0.38
Nickel ..	12.7	0.106	5.9	1460	—	0.14
Platinum ..	8.8	0.032	6.2	1770	27	6.17
Silver ..	18.5	0.055	5.9	960.5	26	1.01
Steel ..	10.0	0.114	—	1300–1400	—	0.06–0.12
Sulphur ..	60.0	0.16–0.24	5.1–7.4	119	10	0.0007
Tantalum ..	7.9	0.036	—	2900	—	—
Tin ..	21.3	0.052	6.4	232	14	0.15
Tungsten ..	3.5	0.034	—	3400	—	—
Vulcanite ..	80.0	0.4	—	—	—	0.0004
Zinc ..	28.6	0.091	6.9	420	28	0.27

Liquids and Gases	Coefficient of Cubical Expansion	Specific Heat about 18° (cal./deg. gr.)	Melting-point, °C.	Boiling-point, °C.	Latent Heat of Vaporization (cal./gr.)
Alcohol, C_2H_5OH ..	0.00110	0.58	–114	78.3	202
Benzene, C_6H_6 ..	0.00124	0.41	+5.5	80.2	94
Carbon disulphide, CS_2 ..	0.00121	0.24	–112	46.2	85
Ether, $(C_2H_5)_2O$..	0.00163	0.56	–123.6	34.6	90
Glycerin, $C_3H_5(OH)_3$..	0.00050	0.58	–20	290	—
Mercury ..	0.000181	0.0333	–38.87	356.7	68
Petroleum ..	0.00092	0.51	—	110–120	75
Turpentine, oil of, $C_{10}H_{16}$..	0.00094	0.42	—	161	70
Water (18° C.) ..	0.00018	0.999	0	100	539.1
Carbon dioxide ..	—	—	–57	–78.5	142
Helium ..	—	—	—	–268.8	—
Hydrogen ..	—	—	–259	–252.8	110
Neon ..	—	—	—	–245.9	—
Nitrogen ..	—	—	–210.5	–195.8	48
Oxygen ..	—	—	–218	–183.0	51

TABLE II.—EXPANSION OF WATER

Temperature	Volume	Temperature	Volume	Temperature	Volume
0° C.	1.000132	7° C.	1.000071	14° C.	1.000729
1	073	8	124	15	0874
2	033	9	191	16	1030
3	008	10	272	17	1198
4	000	11	367	18	1377
5	008	12	475	19	1567
6	032	13	596	20	1768

TABLE III.—SPECIFIC HEAT c_p OF GASES, AND RATIO $\gamma = c_p/c_v$

	c_p at 18°	$\gamma = c_p/c_v$
Air.	0.241	1.40
Alcohol	0.4534	1.15
Argon	0.127	1.65
Carbon dioxide . .	0.202	1.30
Ether	0.4280	1.09
Helium	1.26	1.66
Hydrogen	3.400	1.41
Iodine	0.0336	1.294
Nitrogen	0.244	1.40
Oxygen	0.218	1.40
Water vapour . . .	0.3787	1.28

TABLE IVa.—VAPOUR PRESSURE OF WATER IN MM. OF MERCURY

t	p	t	p	t	p	t	p
0° C.	4.6	70	233.5	140	2,711	220	17,400
10	9.1	80	355.1	150	3,571	240	25,110
20	17.4	90	525.8	160	4,636	260	35,200
30	31.8	100	760	170	5,941	280	48,120
40	55.3	110	1074.6	180	7,521	300	64,460
50	92.5	120	1489.2	190	9,415	320	84,720
60	149.2	130	2026.3	200	11,662	340	109,600

TABLE IVb.—VAPOUR PRESSURE OF WATER IN KG./CM.²

<i>t</i>	<i>p</i>	<i>t</i>	<i>p</i>	<i>t</i>	<i>p</i>	<i>t</i>	<i>p</i>
99° C.	1	158	6	183	11	200	16
119	2	164	7	186	12	203	17
132	3	169	8	190	13	206	18
142	4	174	9	194	14	209	19
151	5	179	10	197	15	211	20

TABLE V.—PRESSURE (IN MM. OF MERCURY) AND DENSITY (IN GR./M.³) OF SATURATED WATER VAPOUR

<i>t</i> °C.	<i>p</i> mm.	<i>ρ</i> g./m. ³	<i>t</i> °C.	<i>p</i> mm.	<i>ρ</i> g./m. ³	<i>t</i> °C.	<i>p</i> mm.	<i>ρ</i> g./m. ³	<i>t</i> °C.	<i>p</i> mm.	<i>ρ</i> g./m. ³
-10	1.95	2.14	0	4.58	4.84	+10	9.2	9.4	+20	17.5	17.3
-9	2.13	2.33	+1	4.9	5.2	11	9.8	10.0	21	18.7	18.3
-8	2.32	2.54	2	5.3	5.6	12	10.5	10.7	22	19.8	19.4
-7	2.53	2.76	3	5.7	6.0	13	11.2	11.4	23	21.1	20.6
-6	2.76	2.99	4	6.1	6.4	14	12.0	12.1	24	22.4	21.8
-5	3.01	3.24	5	6.5	6.8	15	12.8	12.8	25	23.8	23.0
-4	3.28	3.51	6	7.0	7.3	16	13.6	13.6	26	25.2	24.4
-3	3.57	3.81	7	7.5	7.8	17	14.5	14.5	27	26.7	25.8
-2	3.88	4.13	8	8.0	8.3	18	15.5	15.4	28	28.3	27.2
-1	4.22	4.47	9	8.6	8.8	19	16.5	16.3	29	30.0	28.7

TABLE VI.—PRESSURE OF SATURATED VAPOURS (IN MM. OF MERCURY)

Temperature	Ether	Carbon Disulphide	Alcohol	Benzene	Water	Mercury
-20° C.	66	47	3.3	6	0.77	
0	185	128	12.5	26	4.6	0.0004
+20	440	298	44.1	75	17.5	0.0011
40	920	618	133.6	182	55.3	0.006
60	1740	1160	351	389	149.2	0.025
80	3000	2030	812	753	355.1	0.09
100	4900	3220	1690	1342	760	0.28
Boiling-point	34.5° C.	46.2°	78.3°	80.2°	100°	356.7°

TABLE VII.—CRITICAL TEMPERATURES AND PRESSURES

	Critical Temperature, °C.	Critical Pressure, Atmospheres		Critical Temperature, °C.	Critical Pressure, Atmospheres
Helium ..	-267.84	2.26	Ammonia ..	133	112
Hydrogen ..	-239.91	12.80	Sulphur dioxide	157	78
Neon ..	-228.91	26.86	Ether	194	35.5
Nitrogen ..	-147.13	33.4	Alcohol	243	63
Oxygen ..	-118.82	49.71	Carbon disulphide	273	76
Methane ..	-82.85	45.60	Benzene	288	47
Ethylene ..	+ 9.5	50.65	Water	374	218
Carbon dioxide	+31.1	73			

TABLE VIII.—HEATS OF COMBUSTION (K-CAL)

Reaction	Per Gramme of Substance Burned	For the Number of Mols O ₂ appearing in the Equation	Remarks
2H ₂ + O ₂ = 2H ₂ O	34.3	137.0	Product liquid
2K ₂ + O ₂ = 2K ₂ O	1.24	194.2	" solid
2Na ₂ + O ₂ = 2Na ₂ O	2.08	192.0	" "
2Ca + O ₂ = 2CaO	3.49	280	" "
2Zn + O ₂ = 2ZnO	1.30	170.4	" "
2Cu + O ₂ = 2CuO	0.584	74.4	" "
4Cu + O ₂ = 2Cu ₂ O	0.32	81.6	" "
2Pb + O ₂ = 2PbO	0.243	100.6	" "
2S + 2O ₂ = 2SO ₂	2.21	141.2	" gaseous
2S + 3O ₂ = 2SO ₃	2.87	183.8	" "
P ₄ + 5O ₂ = 2P ₂ O ₅	5.96	740	" solid
2N ₂ + O ₂ = 2N ₂ O	-0.631	-35.4	" gaseous
N ₂ + O ₂ = 2NO	-1.64	-43.2	" "
N ₂ + 2O ₂ = 2NO ₂	-0.142	- 4.0	" "
2N ₂ + 5O ₂ = 2N ₂ O ₅	-0.043	- 2.4	" "
2C + O ₂ = 2CO	2.17	52.2	Diamond, product gaseous
C + O ₂ = CO ₂	7.86	94.3	" " "
C + O ₂ = CO ₂	8.0	97	Amorphous, " "
C + O ₂ = CO ₂	7.9	95	Graphite, " "

EXAMPLES

HEAT

CHAP. I (pp. 1-34)

1. How can the coefficient of expansion of a solid body in the form of a rod be measured?

By how many degrees must a piece of iron be raised in temperature so that its volume will increase by a thousandth part of itself?

(Coefficient of linear expansion of iron = 0.000012 .) (*Liv. Inter.*)

2. How have you determined the specific heat of a metal? What precautions would you have to take if you wished to make a more accurate determination?

What evidence can you give for the assumption which you use in the calculation, viz. that the heat absorbed by a quantity of water is proportional to its rise of temperature? (*Liv. Inter.*)

3. Describe an accurate method of measuring the specific heat of a solid. Discuss the general nature of the results of experiments to determine the atomic heats of elements. (*C. Tripos, Pt. I.*)

4. Explain carefully why a gas has two principal specific heats.

Describe a method of measuring each experimentally. (*Liv. F.*)

5. A boy eats 0.5 kgm. of ice at 0° C. in 10 minutes. What horse-power does he expend if his body temperature is 98° F.?

746 watts = 1 h.p. Latent heat of ice = 80 calories/gramme. (*Br. Inter.*)

6. Describe one of the more accurate methods of determining the mechanical equivalent of heat.

Given that the mean radius of the earth is 6400 km. and its mean specific heat is 0.1 , find the rise in temperature the earth would experience if its energy of rotation were suddenly transformed into heat.

1 calorie is equivalent to 4.2×10^7 ergs. (*Br. F.*)

7. State clearly the meaning of the term "mechanical equivalent of heat".

The difference in temperature between the top and bottom of a waterfall 200 metres high is 0.4° C. Assuming that all the heat developed remains in the water, deduce a value for the mechanical equivalent of heat. (*Br. Inter.*)

8. In what way has it been shown that heat is a form of energy?

A loaded cart weighing 2 tons runs for half a mile down a hill, the gradient of which is 1 in 20 . At the foot of the hill its velocity is 20 feet per sec. Find approximately the amount of heat developed by friction during the descent.

(Neglect the kinetic energy of rotation of the wheels.)

$g = 32$ ft./sec.². One water lb. degree centigrade unit of heat = 1390 foot-pounds. (*Br. Inter.*)

9. Explain why the specific heat of a gas at constant pressure differs from the specific heat at constant volume.

Show how this difference in the specific heats of a gas has been used to estimate the value of the mechanical equivalent of heat. *(Br. Inter.)*

CHAP. II (pp. 35-64)

10. Outline the essential features of the kinetic theory of gases and apply it, so far as you can, to account for the laws of Boyle, Avogadro, and Charles. *(London Ext.)*

11. What do you understand by the "mean square velocity" of the molecules of a gas? Describe how it can be calculated, proving any formula you use.

If the root mean square velocity of an oxygen molecule at N.T.P. is 461 m. per second, what is that of a hydrogen molecule (*a*) under the same conditions, (*b*) at 100° C.? *(Sheffield Inter.)*

12. Show how, on the kinetic theory of gases, the pressure depends upon the molecular mass and velocities.

Show that, on this theory, all perfect gases will have the same coefficient of expansion. *(Liv. F.)*

13. Give an account of the simple kinetic theory of gases and deduce a value of the mean square of the molecular velocity. Explain how Boyle's law follows from this theory. *(C. Tripes, Pt. I.)*

14. Show how the gravitational constant *G* has been accurately determined.

To what temperature must the surface of the moon be raised in order that hydrogen molecules may escape, if it be supposed that all the molecules have the energy corresponding to the temperature of the surface?

Mass of moon = 7×10^{25} gm.; radius of moon = 1760 km.

Gravitational constant = 6.7×10^{-8} ; *R* = 2 calories. *(Oxford F.)*

15. Describe a method of determining the ratio of the two specific heats of a gas. What inferences concerning the constitution of the molecules of a gas have been drawn from the value of this ratio? *(C. Tripes, Pt. I.)*

16. Explain why the specific heats of a gas at constant pressure and at constant volume differ, and show that for a gas whose molecules have each *n* degrees of freedom

$$\frac{C_p}{C_v} = 1 + \frac{2}{n}.$$

Describe some experiment by means of which this ratio has been determined. *(Manchester, H. Pt. I.)*

17. Describe the methods of measuring the atomic heats of metals at low temperatures.

Suggest the outlines of a theory which gives results corresponding closely with experiment. *(Ox. F.)*

18. Describe an accurate method for the determination of the specific heat of a solid at low temperatures. State briefly the results of the examination of specific heats of solids over a wide range of temperatures. *(Lond. Inter.)*

19. Derive an expression for the coefficient of viscosity of a gas. *(Lond. Inter.)*

20. Describe the main theoretical and experimental investigations of the Brownian movement.
(*C. Tripos, Pt. II.*)

21. Survey the methods, based on the kinetic theory, of determining Loschmidt's number.
(*Lond. Exter.*)

22. How may the value of the mean free path of a gaseous molecule be deduced from (1) the coefficient of diffusion, (2) the coefficient of viscosity of the gas?

Give a short account of experiments on Brownian movements. (*Br. F.*)

23. Explain in terms of the molecular theory of matter (1) the phenomenon of diffusion, (2) the spherical form of a drop of water, (3) evaporation.

(*Br. Inter.*)

24. Explain what is meant by *osmotic pressure* and describe how it may be measured.

A solution of barium chloride (BaCl_2) containing one-tenth of a gramme-molecule per litre has an osmotic pressure of 4.48 atmospheres at 17°C . Find the percentage of the salt which is dissociated.

(1 litre of hydrogen at N.T.P. weighs 0.089 gm.) (*C. Tripos, Pt. I.*)

CHAP. III (pp. 65-91)

25. Describe a form of calorimeter which depends in its action upon the change of volume which results when ice melts.

An iron ball, of weight 160 gm., and at 100°C ., is brought to 0° by immersing it in a mixture of ice and water contained in a thermally insulated vessel. Find the change in volume of the mixture, given that the specific heat of iron is 0.10 and that the density of ice is 0.92. (Latent heat of ice = 80 calories per gramme.)

(*Br. Inter.*)

26. Describe and explain the action of the Bunsen ice calorimeter.

(*Br. Inter.*)

27. Show from thermodynamical reasoning that a substance which contracts on melting has its melting-point lowered by an increase in the pressure.

Calculate from familiar data the freezing-point of water at a pressure of 50 atmospheres.

(*Br. P. & Hons., Pt. I.*)

28. What is meant by the term "latent heat"?

Steam at 100°C . is passed into a mixture of ice and water at 0°C . How much ice will be melted when 10 gm. of steam have been condensed?

Latent heat of fusion of ice = 80 centigrade units.

Latent heat of evaporation of water at 100°C . = 537 centigrade units.

(*Br. Inter.*)

29. How may the temperature of saturated water vapour be determined for a series of pressures below that of the atmosphere?

On a certain day the actual temperature is 15°C . and the dew point is 6°C . Calculate the relative humidity and indicate how the mass of water vapour in 1 litre of air could be estimated.

Saturated vapour pressure at 6°C . = 7.0 mm. of mercury.

" " " 15°C . = 12.7 " " (*Br. Inter.*)

30. Explain what is meant by the "triple point" for a substance.

Show on a *pv* diagram the general shape of the isothermals near the triple point of a substance (a) which expands on melting, (b) which contracts on melting.

Explain the state of the substance denoted by various portions of the isothermals.

(*Br. F.*)

31. A cylindrical vessel contains a mixture of air and saturated water vapour. The pressure of the mixture is 780 mm. of mercury, the partial pressure of the vapour being 20 mm. What is the pressure when the volume of the vessel is reduced to one-half of its original volume at constant temperature?

(*Br. Inter.*)

32. Describe carefully a method of determining the vapour density of an unsaturated vapour (ether, for example), giving the necessary calculations.

(*Sheff. Inter.*)

33. What is meant by the saturated vapour pressure of a liquid? Explain how it is related to the boiling-point.

A cylinder provided with a frictionless movable piston contains air and a small amount of water. When the temperature is increased from 7° C. to 47° C. the distance of the piston from the closed end of the cylinder increases by 25 per cent, the external atmospheric pressure on the piston remaining constant throughout and equal to 76 cm. Assuming that the saturated vapour pressure of water at 7° C. is 1 cm., calculate its value at 47° C.

(*Man. H.*)

34. Give drawings of the isothermal curves for carbon dioxide (liquid and vapour) in the neighbourhood of its critical temperature. By what experimental means are such curves obtained? How will they be altered if the gas is not pure but contains a small proportion of air?

(*Liv. F.*)

35. Discuss, with diagrams, the form of the isothermals of a substance above and below its critical temperature.

Explain briefly the principles underlying some method of liquefying gases such as air.

(*Man. H.*)

36. Write a short account of the simple physical properties of gases and vapours.

(*Liv. Inter.*)

37. Describe the experiments which have been made, and the results which have been obtained, on the relation between the pressure, volume, and temperature of a gas.

How have the deviations from the simple laws been explained?

(*C. Tripos, Pt. I.*)

CHAP. IV (pp. 92-173)

38. Obtain a relation connecting the pressure and volume of a given mass of gas which is subjected to an adiabatic change.

Calculate the rise in temperature of a quantity of gas, initially at a temperature of 15° C., if its pressure is suddenly doubled ($\gamma = 1.4$). (*Man. H.*)

39. Show that the external work done by a body during expansion is given by the expression $\int_{v_1}^{v_2} p dv$ in the usual notation.

Find from the following data how much of the specific heat of hydrogen at constant pressure is due to the external work done in expansion.

1 gm. of hydrogen at a pressure of 76 cm. of mercury at 0° C. occupies 11.2 litres.

Specific gravity of mercury = 13.6. $J = 4.2 \times 10^7$ ergs/calorie.

40. A gas expands under conditions which prevent heat from entering or leaving it. Discuss the two limiting cases:

(a) a very slow expansion;

(b) expansion into a region of low pressure, so that the external work done can be taken as negligible.

Explain very briefly the bearing of (b) on the problem of producing low temperatures.

(*C. Tripos, Pt. I.*)

41. Describe and discuss the porous plug experiments of Joule and Kelvin. Explain what is meant by *temperature of inversion*, illustrating your answer by reference to hydrogen or helium. (*Lond. Exter.*)

42. Give an account of the principle governing the action of a refrigerating machine.

Explain why the large heat content of the earth is not used as a source of energy. (*Liv. F.*)

43. Give an account of the methods of liquefying gases, and discuss the principles on which these methods depend. (*C. Tripos, Pt. I.*)

44. Explain what is meant by a reversible change.

Show that the efficiency of all reversible engines working between the same two temperatures is the same. (*C. Tripos, Pt. I.*)

45. State and explain the second law of thermodynamics, and show how it can be used to define an absolute scale of temperature. (*C. Tripos, Pt. I.*)

46. Assuming the properties of a Carnot engine, show how a scale of temperature may be devised which is independent of the properties of any particular substance. What fixes the zero of such a scale?

How may this absolute scale be realized approximately in practice? (*Man. H.*)

47. Define the term "entropy".

What is meant by the statement that the entropy of a system tends to a maximum?

What change of entropy occurs when 50 gm. of steam at 100°C . are converted into water at the same temperature?

Latent heat of steam = 536. (*Br. F.*)

48. Define "entropy" and show that the change in entropy of a self-contained system in passing from one state to another depends only upon the initial and final states. Show also that the entropy of a system is increased by processes which tend to equalize the temperatures of its parts. (*Man., H. Pt. I.*)

49. What are the conditions which must be fulfilled by an ideal heat engine? Point out some of the ways in which an actual steam engine fails to fulfil these conditions.

Show that the Carnot engine is the most perfect possible engine, and calculate the efficiency of that engine when working between the temperatures 100° and 10°C . (*Br. F.*)

CHAP. V (pp. 174-184)

50. Draw a diagram of a typical hot-water system of a house.

In a certain hotel it is found that every time a hot bath is taken by a visitor 15 lb. extra of coal have to be fed to the fire under the boiler of the hot-water system to restore the initial conditions. Using the following data, calculate the percentage of the available heat which is used. Give two causes of the low value obtained.

Heating value of coal = 8000 lb. $^{\circ}\text{C}$. units per lb.

Weight of iron bath = 224 lb.

Specific heat of iron = 0.11.

Weight of water used = 300 lb.

Temperature of supply water = 10°C .

Final temperature of water in bath = 38°C .

(*Sheff. Inter.*)

51. Describe a method of finding the thermal conductivity of a good conductor.

A long metal bar is coated with wax, and one end of the bar is maintained at a temperature above the melting-point of the wax. If Newton's law of cooling holds, show that when the steady state is reached the length of the portion of the bar on which the wax is melted is proportional to the square root of the thermal conductivity.
(*C. Tripos, Pt. I.*)

52. What is meant by the coefficient of thermal conductivity?

The walls of a cottage are 12 cm. thick and are built of material of conductivity 0.0035. The temperature inside the cottage is kept by fires at 15° C., the outside temperature being 5° C. The area of the walls is 1000 sq. m. What is the minimum amount of coal of calorific value 8400 cal. per gm. that must be burnt per hour in order to maintain a constant temperature of the interior?

(*Br. Inter.*)

53. Describe a method suitable for finding the thermal conductivity of a liquid.

Discuss the difficulties which beset the investigation of the thermal conductivity of gases and indicate how and to what extent they have been overcome.
(*Lond. Exter.*)

VIBRATIONS AND WAVES

CHAPS. I, II (pp. 189-249)

54. What do you understand by simple harmonic motion?

A beam of light falls on a screen after successive reflections from two small mirrors attached to the prongs of two tuning forks vibrating in perpendicular planes, the frequency of one fork being nearly twice that of the other. Describe and explain the figures produced on the screen.
(*Br. Inter.*)

55. Show that the energy in a train of progressive sound waves is half potential and half kinetic.

Find an expression for the energy conveyed by sound waves, and show how the amplitude of vibration necessary for audibility has been determined.

(*Br. F.*)

56. Show that the velocity of propagation of longitudinal waves in a uniform rod is $\sqrt{E/\rho}$, where E is Young's modulus for the rod and ρ is its density.

A uniform rod is suspended vertically, being clamped at its upper end. Find how the elongation produced by its weight varies with its length.

(*Man., H. Pt. I.*)

57. Prove that the elasticity of a gas for adiabatic compressions is γp , where γ is the ratio of the specific heat and p is the pressure.

(*Ox. F.*)

58. An observer sets his watch by the sound of the university bell one mile away. Find the allowance that he should make on account of the distance, the temperature of the air being 20° C.

(Velocity of sound at 0° C. = 1080 feet per second.)

(*Br. Inter.*)

59. Find an expression for the velocity of sound in a gas in terms of the elasticity and density of the gas.

Two trains of waves of the same form, amplitude and wave-length traverse the same region of space in opposite directions. Show that they lead to the formation of nodes and loops.

(*Lond. Inter.*)

60. Discuss the principles involved in the use of a stroboscope.

In order to test the speed of a gramophone turntable there is placed upon it a disc marked with 36 equally-spaced radial lines. When this disc is viewed in the light from a lamp served from the alternating current mains of frequency 50 per second it appears, while the table is rotating, to be stationary. Find the possible values of revolutions per minute of the turntable. (*Leeds Inter.*)

61. Light from an arc-lamp is focused at a point near the circumference of a cardboard disc in which are cut 30 equally-spaced holes, so that the light is alternately transmitted and interrupted when the disc rotates. A vibrating tuning fork appears to be motionless when viewed by the light transmitted if the disc makes 250 revolutions per minute. Explain this phenomenon.

How many beats would be heard per second if this fork were sounded simultaneously with one of frequency 128? (*Sheff. Inter.*)

62. Show that the resultant of two wave-motions of equal wave-length and amplitude travelling in opposite directions is a system of stationary waves, and deduce an equation for the resultant motion.

How could the velocity of sound in a gas be deduced from observations on such a system of stationary waves? (*Br. P.*)

63. Compare the characteristics of progressive and stationary waves.

Describe methods of producing stationary waves in which the vibrations are (a) transverse, (b) longitudinal. How would you show the presence of nodes and antinodes in each case? (*C. Tripes, Pt. I.*)

64. Discuss the application of the method of dividing a wave-front into Fresnel zones to diffraction phenomena, illustrating your answer with particular examples. How many half-period elements are there in a circular portion, 1 cm. radius, of a plane wave-front, given that the wave-length is 6×10^{-5} cm. and the distance of the point of observation from the wave-front 1 metre?

(*Man., H. Pt. I.*)

SOUND

CHAPS. I, II (pp. 251-287)

65. Describe a method of measuring the frequency of the note emitted by a tuning fork.

Two stretched wires A and B, each of the same metal and under the same tension, emit the same note when plucked. The length of A is 3 ft. and its diameter is half that of B. What is the length of B? If the tension in B is doubled, to what length must it be adjusted to give again the same note as A? (*Br. Inter.*)

66. Prove that the velocity of a pulse along a stretched string varies directly as the square root of the tension and inversely as the square root of the linear density.

Calculate the frequency of the fundamental note of a string 1 metre long, weighing 2 gm., when stretched by a weight of 100 kilogrammes. (*Br. F.*)

67. Discuss the terms *loudness*, *pitch*, and *quality* as applied to a musical note. Account for the difference in quality of the notes given by a closed and an open organ pipe. (*Leeds Inter.*)

68. Discuss the character of the vibrations of a uniform rod clamped in the middle and stroked with a resined cloth. The rod being 2 metres long, of metal of density 7 and of Young's modulus 10^{12} C.G.S., find the pitch of the vibration of lowest frequency and that of the next lowest. *(Br. P.)*

69. Describe a simple form of singing flame. Account for its behaviour in maintaining a column of air in vibration. *(Lond. Inter.)*

70. Draw an analogy between the possible modes of vibration of a stretched wire and of a column of air. Give an explanation of the difference in quality between a closed and an open organ pipe. *(Br. Inter.)*

71. Explain why the sound of a large explosion has only a limited range of audibility in the immediate neighbourhood of the explosion, and why, also, there is a second zone of audibility at a great distance from the source, with a silent zone inside. What evidence can be obtained about the upper atmosphere from observations of sound in these regions? *(Ox. F.)*

72. Explain Doppler's principle.

A spectrum line, of wave-length 4×10^{-5} cm., in the spectrum of the light from a star is found to be displaced from its normal position towards the red end of the spectrum by an amount equivalent to 10^{-8} cm. What velocity of the star in the line of sight would account for this? *(C. Tripos, Pt. I.)*

73. Describe some experiments illustrating the reflection and refraction of sound.

The sides of a certain mountain pass assumed to be vertical are 1 mile apart. A man in the pass fires a gun and hears the first two echoes, one from each side, 4 seconds apart. Where is he with respect to the sides?

(Velocity of sound = 1100 ft./sec.)

(Br. Inter.)

74. A vibrating tuning fork tied to the end of a string 6 ft. long is whirled round in a circle. If it makes two revolutions a second, calculate the ratio of the frequencies of the highest and lowest notes heard by an observer situated in the plane of the tuning fork.

(Velocity of sound = 1100 ft./sec.)

(Man. H.)

ANSWERS TO EXAMPLES

1. 27.8°C . 5. 0.55 h.p. 6. 103.1°C .
7. 4.90×10^7 ergs per calorie. 8. 405 lb. $^{\circ}\text{C}$. units.
11. 1844 metres per second; 2155 metres per second.
14. 150°C . 24. 43.8 per cent. 25. A contraction of 1.74 c.c.
27. -0.34°C . 28. 79.6 gr. 29. 55.1 per cent.
31. 1540 mm. of mercury. 33. 7.45 cm. of mercury.
38. 76.9°C . 39. 0.99 calories/gr. 47. 71.8 calories/ $^{\circ}\text{C}$.
49. 0.24. 50. 7.57 per cent. 52. 12.5 Kg.
56. Elongation varies as L^2 where L is the original length. 58. 4.72 secs.
60. $166.7n$ rotations/min. where n is an integer. Note that the frequency of occurrence of the maximum illumination from the lamp is 100/sec.
61. Frequency of fork must be $125n$ vibrations per second, where n is an integer. If $n = 1$ there will be a beat frequency of three per second.
64. 167. 65. 1.5 ft.; $\frac{3}{\sqrt{2}}$ ft. 66. 350 cycles/sec.
68. 945 cycles/sec.; 2835 cycles/sec.
72. A velocity of recession of 75 km./sec.
73. 1540 ft. from one side. 74. 1.147 : 1.

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